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FREEZING POINTS OF SOILS AT THE MOISTURE EQUIVALENT

A Thesis submitted to the Faculty of the Graduate School of
The University of Minnesota

BY

REUBEN MARION PINCKNEY

In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

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R. M. Pinckney.

University of Minnesota.
Division of Soils.
Nov. 5, 1924.

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INTRODUCTION.

The importance of the relation between the soil and its contained water has long been recognized, and methods to improve our understanding of this have been persistently sought. In the past few years those based upon the freezing of the water held in the soil have attracted much attention because of their novelty, and even more because of some of the conclusions reached by their advocates.

The values directly measured by these methods are the temperatures at which freezing of the soil water, as it exists in the soil, takes place, and the expansion which it undergoes on freezing. Some investigators claim that these methods furnish information as to the total salt content of soils (21), the uniformity or otherwise of the soil solution (11), the quantity and concentration of the soil solution available to plants (19, 20), the nature of acidity as well as the lime requirement of soils (6), the physical classification of the water contained in the soil (12), the effect of fertilizers and soil amendments (20), the effect of cultivation and cropping upon the soil, and the time required to overcome this (31), and the rate and extent of solubility of the soil material (14).

Bouyoucos and his collaborators who developed these methods, recognized a connection between the texture of the soil and the values secured by freezing. They ascribed this connection to the greater solubility of the finely divided matter of the soil, and did not regard it as at all impairing the validity of their conclusions. The work of Keen, Parker and Fisher indicate that the texture of the insoluble soil material has an effect upon the two measurements used as the basis of his deductions by Bouyoucos other than merely upon the solubility of the soil material and that this must be taken into account before these measurements may be used in the study of the relation between soil and soil water.

The moisture equivalent is among the most convenient methods of expressing the texture of soils in comparable form. If a direct connection between the freezing point and the moisture equivalent is established it will be evident that the texture of a soil directly affects its freezing point. The experimental work reported below was undertaken to learn to what extent, if any, such a connection exists.

SOIL WATER.

The water carried by soil, according to the most commonly accepted view, is present either entirely as hygroscopic water, or partly as hygroscopic and partly as capillary water, or, lastly, partly as hygroscopic, partly as capillary, and partly as gravitational water.

The hygroscopic water is held by the soil in the form of a thin film covering the surface of every solid particle. If not otherwise supplied it would be absorbed, until equilibrium was reached, from

the more or less moist air in contact with the soil. Hygroscopic moisture does not move from one particle to another as liquid water, but as water vapor and through the surrounding atmosphere.

The capillary water is held in part as thicker films surrounding the soil particles, and in part collected in the angles between the particles where they touch, forming annular wedges about the points of contact and completely occupying some of the open spaces, first filling the smaller ones. The thickness of its films is thus far less uniform, and in consequence its amount is not directly proportional to the total soil surface. The force, surface tension, which determines the movement of the capillary water prevents its responding to gravity, but the water will move from wetter to drier portions of the soil, and this adjustment becomes more rapid as the thickness of the water films increases.

The gravitational water is still farther removed from direct contact with the soil particles and thus less attracted by them. It occupies the larger open spaces, and is hardly to be regarded as in film form. It moves downward in response to gravity, but if it comes into contact with soil not fully supplied with capillary water it will spread over the surfaces of the soil particles, changing partly or wholly into this form.

BOUYOUCOS' PROPOSED CLASSIFICATION OF SOIL WATER.

Bouyoucos (12) has proposed a quite different classification of the soil water, dividing it into free* and unfree water, with the latter subdivided into capillary-absorbed and combined water. His scheme is as follows:

1: Free water*: Water that is sufficiently free from the influence of the solid soil particles to freeze readily (between 0.0°C. and -1.5°). Bouyoucos considers this portion only as able to dissolve soluble matter, and hence to form the soil solution. It would include all the gravitational water, defined as above, as well as part of the capillary water, in any sample of soil.

2: Unfree Water: That portion of the water carried by any soil that does not freeze readily (i.e. remains unfrozen at -1.5°C). It includes the remainder of what is commonly designated capillary water as well as all of the hygroscopic water, and is subdivided into:

---

* There is much confusion in the use of the term free water. Most writers on soil subjects, being comparatively uninterested in the availability of the soil moisture to plants, have used the term as synonomous with gravitational water - the portion free to drain away. Hilgard and Loughridge (1, P. 13), at least as early as 1874, first used it to designate the water present in excess of the hygroscopic coefficient - the approximate amount free for the use of plants. Alway and his co-workers have used it in the same sense. Now Bouyoucos proposes to employ the same term to indicate that part of the soil water that is free to freeze readily.

Capillary absorbed water (or water of solid solution) and combined water (water of hydration). The former consists of the portion that freezes between -1.5° and -4.0°, and the latter of what remains unfrozen at -4.0°.

Bouyoucos (8) recognizes that his limits of -1.5° and -4.0°C are arbitrary. In an earlier paper he stated that his combined water was about equal to the wilting coefficient of Briggs and Schantz, but later work (12) led him to conclude that there is no close relation between combined water and either wilting coefficient, hygroscopic moisture, or moisture equivalent. He concluded that repeated freezing and thawing of a moist soil is able to change into free water some of the capillary absorbed water, but none of the combined water.

Bouyoucos assumed that the capillary absorbed water dissolves nothing, and that the combined water is already in a solid state, he failing to find any evidence of its freezing even when the temperature is reduced as low as -78°C.

FREEZING POINTS OF MOIST SOILS.

The depression of the freezing point of a solution is proportional to the concentration of ions and undissociated molecules together, and for water is 1.86°C. per mol concentration. This provides a reliable method for the determination of the concentration of solutions in which the solute is known. In the case of electrolytes it shows the apparent molecular weight, and thus the degree of dissociation. In the case of mixed solutions, or those of unknown composition, freezing point determinations give the concentration in terms of moles but not of percentage or weight of solutes. Bouyoucos has attempted to apply these relationships to the study of the concentration of soil solutions.

Bouyoucos (19) was the first to actually determine the freezing points of soils, or even to suggest that it might be useful to do so. Little or no attention had previously been paid to the temperature at which the freezing of moist soils actually occurs, although many investigators had mentioned effects of freezing upon the physical and chemical properties of soils which they either observed ar assumed. It seemed to be tacitly assumed that the soil water freezes just as it would if removed from the soil. For several years previous to beginning his study of freezing points Bouyoucos had been studying the temperature of soils, and its effect upon certain of their properties. He had observed the influence of varying amounts of water upon changes in the temperature and also upon the temperatures at which soils, both in the laboratory and exposed in the field, remained unfrozen. Since 1915 he and his associates have done a great deal of work upon the freezing points of soils, on the general assumption that the soil solution when in the soil freezes exactly as it would if it were first removed without change in concentration, an assumption they have not supported by experimental evidence.

By his method (20) as finally developed, the soil, brought to the desired degree of moistness, is placed in a glass freezing point tube, usually a 1 inch x 8 inch test tube. Into this a Beckman thermometer , previously set so that the freezing point of water comes somewhat above the center of the scale and is accurately known, is inserted until the bulb is completely surrounded by the moist soil. The whole is placed in a freezing bath of water, ice and salt, in such proportions that the temperature of the freezing bath is two or three degrees lower than the freezing point of the soil. When both soil and thermometer have cooled to about the freezing temperature, the tube is removed from direct contact with the freezing mixture, and cooled more slowly in a cold air chamber of metal set permanently into the freezing bath. This is enough larger than the freezing point tube to insure that the latter comes into contact with only the cold air and not with the metal. The slower cooling is continued until such a temperature is reached that freezing can be induced by a slight jar or by friction, for which the rotation of the thermometer a few degrees backward and forward so as to rub the undercooled soil is usually sufficient. When the freezing begins the temperature rises rapidly to the freezing point, remains near this for some time, then slowly falls. The highest point reached in the rise is recorded as the freezing point. The drier the soil the greater is the degree of undercooling found necessary and the shorter the time the mercury remains at this maximum point.

Bouyoucos believes that the freezing point so determined depends only upon the concentration of the soil solution as it exists in the soil, and that that concentration can be computed directly from it.

Although the method may appear essentailly the same as the more familiar one for liquids, it should be pointed out that there are some very important differences. One is that the temperature of the soil mass cannot be kept uniform throughout by stirring, a second is that while in liquids the pressure exerted upon the bulb of the thermometer is uniform at all points (within very close limits), such is not necessarily the case in the freezing of moist soils. Bouyoucos recognized the latter, but did not regard it as a serious objection. (19).

Although the freezing point depressions of solutions in mass are proportional to their concentration, and by analogy a soil frozen with varying amounts of water should show deprressions inversely proportional to those amounts, Bouyoucos (19) observed that such was not the fact with soils, but that the depression increased more rapidly that the percentage of water decreased. To explain this unexpectedly rapid increase he proposed his hypothesis of "unfree" water mentioned above, assuming that this "unfree" water both is unable to take part in dissolving the soluble matter, and so does not form part of the volume of the solution, and does not freeze.

His hypothesis assumes that all the soluble matter is dissolved in the "free" portion of the water. The latter being less in amount

than the total water, the solution is more concentrated than if the whole of the water functioned as a solvent.

He found that different soils when frozen with like amounts of added water had very different freezing points, the finer textured ones showing the greater depression. This he considered conclusive evidence that their solutions were more concentrated, and accordingly that the finer textured soils were either richer in soluble matter, or were able to cause more water to become "unfree", or more probably both.

To fix an empirical relationship between soluble matter and observed freezing point depression, he froze aqueous extracts of soils, portions of the extracts being then evaporated to dryness to determine the dissolved matter. As a result of a number of such determinations (19) he concluded that a depression of 0.0032°C indicates 100 parts dissolved matter per million parts of water. In a later paper (20) he arrived in a similar way at a value 0.0040°C = 100 parts per million. On the basis of this empiric value he computed from the observed freezing point depressions of moist soils the concentration of the solutions of a great number of soils, and concluded that the concentration varied greatly, and was much greater than previously had been generally supposed. He found a minimum moisture content, below which a soil could not be frozen, this varying with the texture of the soil, and stated that this limit corresponded approximately to the wilting point as determined by Briggs and Shantz (27). He observed that with successive freezing and thawing of the same sample of moist soil the depression became less, and devised a method for measuring the volume of the "unfree" water by measuring the expansion of a soil when frozen in a dilatometer.

PARKER'S WORK ON THE FREEZING OF SOILS AND SOIL SOLUTIONS.

Parker (39), (40) in 1921 reported studies of the freezing points of soils, using benzene and nitro-benzene as well as water. He confirmed Bouyoucos' observation that with water the depression of the freezing point increased much more rapidly than the moisture content decreased, and further found that the same generalization holds true, when any of the three liquids are frozen in other finely divided, insoluble and inert solid materials, of which he used aluminum oxide and silica, but offers a very different explanation. He holds that when the ratio of liquid to solid is low, the force of adhesion between liquid and solid causes a depression of the freezing point of liquids in finely divided solids, even when no soluble material is present. Accordingly the depression of the freezing point of a moist soil that has not been freed of its dissolved material by washing would be additive, being due partly to the solid insoluble portion of the soil and partly to the material in solution. With this interpretation it was evident that the concentration of the soil solution cannot, except at very high moisture contents, be measured by the freezing point method, because the use of the latter assumes that the finely divided material of the soil does not affect the

freezing point of the soil solution. However, if the depression due to the finely divided solid matter could be determined and this subtracted from the observed freezing point depression, the concentration of the soil solution could then be determined.

Parker determined the freezing point depression of 12 washed samples at their moisture equivalents, these consisting of 8 mineral soils, one peat soil and of kaolin, silica, and aluminum oxide.

He took 100 g. samples of each, washed these with 1200 to 1500 cc. of distilled water to remove soluble matter, after which the samples were dried at 105°C, and the moisture equivalent determined in the usual manner. After centrifuging the freezing point determination was made, but he does not state whether the same portion used for the freezing point determination was later used for the determination of the moisture content of the centrifugal material, or whether separate portions were used for the two determinations.

He found that for these samples at the moisture equivalent the freezing point depression due to solid matter was nearly constant, about 0.050°C.

He attributes the depression in excess of this constant to dissolved matter. Hence a determination of the moisture equivalent of a soil and of its freezing point at that moisture content would permit the calculation of the salt content. He points out, however, that it would be both more convenient and more accurate to make the determination at moisture contents above saturation, and so entirely eliminate the depression caused by the solid material. (See Table A).

Table A.
Freezing point depressions of washed soils at their moisture equivalents as found by Parker*.

Soil	Moisture Equivalent.	Freezing Point Depressions.
Plainfield sand	4.73	0.076
Fine sandy loam	12.49	.057
Mellon loam	16.39	.053
Silica	19.14	.057
Aluminum oxide	21.56	.043
Carryington silt loam	21.57	.055
Superior clay	21.84	.061
Knox silt loam	25.40	.057
Miami silt loam	26.47	.052
Silty clay loam	33.29	.061
Kaolin	38.12	.046
Peat	111.60	.061

*(From Parker, F. W.) Soil Science XII, P.228 rearranged).

For the purpose of removing the soil solution from the solid matter in order that its composition and properties might be studied, Parker (39) used Ischerekov's alcohol displacement method and confirmed the latter's conclusion that in this displaced solution the concentration of at least some solutes is the same as before the removal. He concluded that although in some respects alcohol is to be preferred, other displacing liquids may be satisfactorily used. He was the first to determine the freezing points of such displaced solutions. Both analysis and freezing point showed that the concentration of the displaced solutions varies inversely as the moisture content of the soils from which they were displaced. The freezing point depression, however, was always less in the solution than in the original moist soil, and the drier the soil the greater the difference. This confirmed his conclusion that the temperature of freezing is determined not only by the concentration of the solution but also by the area of the surfaces over which the solution is spread as film. From the inverse relationship between the concentration of the displaced solution and the total moisture content of the soil it was evident either that Bouyoucos' "unfree" water is displaced from the soil and dilutes the solution, or that as Parker concluded there is no such "unfree" water. In some cases he was able to displace an aqueous solution from soil so dry that all the water present should have been "unfree".

Bouyoucos in his reply (15) to Parker's articles seemed to admit his inability at that time to disprove the latter's explanation of the observed freezing point depression, but seemed not to accept it completely. He pointed out, as a result of more recent work, (16) that while soils below the saturation point show less depression at freezings subsequent to the first, the original greater depression is restored if the soil is gently stirred before the final freezing. He explains that the freezing causes a movement of water from the smaller to the larger capillaries.

In spite of the work above mentioned, as well as that of Fisher, he still employs the term "unfree" water in the same sense as before. (See "Heat of Wetting as a new means of estimating the colloidal material in soils", by George John Bouyoucos, in Science, Oct.3,1924.)

WORK OF HOAGLAND, BURD and MARTIN.

Hoagland (31) in 1918 reported freezing point determinations on 14 soils which were used by him and his co-workers in a series of soil-tank experiments. The freezings were made upon the soils before the crop was planted, at intervals during its growth and after it had been harvested, and the results compared with those from the analysis of water extractions of the same soils, which were reported at the same time by Burd (23). He accepted Bouyoucos' hypothesis of unfree water, and devised a method for the computation of the amount in any soil without the use of the dilatometer, something that Bouyoucos had not been able to do. Hoagland computed this value from the freezing points of the same soil at two different moisture contents, one about 5 per cent greater than the other. He repeated the determination of Bouyoucos' empiric factor and arrived at the same value, 0.0032°C.

He compared the freezing points of cropped and uncropped soils, and found that the depression was less after cropping, and that it remained less for at least 8 months after the crop had been harvested, while incubation of the moist soil increased the depression. There was very good agreement between the freezing point determination and the amounts of dry matter found by evaporating the water extracts, although he concluded from the freezing points that only about one half the soluble matter found in the 1.5 water extracts had been in solution before the extraction.

Although Hoagland's paper reported many determinations of the freezing points of soils, together with the amount of water in the soil, in the case of the finer textured soils, most of them were lower than the moisture equivalent, which Burd (23) reported for the same soils, while in the coarser ones it was higher. He seems to have followed Bouyoucos' practice, and used an arbitrary convenient amount of water, which is greater for fine soils than for coarse ones, but used no exact system in deciding just how much water should be present. Such samples as were frozen with amounts of water approaching the moisture equivalent have been selected from his paper for presentation in table No. B. As the freezing point changes so rapidly with change in moistness the number is limited to those with water less than .6% away from the moisture equivalent. The data are quoted to show that the depression ranges from very low to moderately high.

Burd and Martin (24) report extensive studies of soil solutions displaced from moist soils by water, in a manner somewhat similar to the alcohol displacement advised by Parker, not however at the moisture equivalent, and often not near that moisture content. Most of their determinations of concentration were made by conductance methods, although freezing points are reported in a few instances, both of the soils and of the solutions displaced from them. Like Parker, they found the freezing point depression of such solutions less than of the soils from which they were displaced. In some cases the difference was small, and in others very large.

Hoagland and Martin (32), as a result of determination of the freezing point on washed aluminum oxide and water, concluded that Parker's belief in the power of merely finely divided solid matter to depress the freezing point is unproved, but admitted that the depression of moist soils is greater than of the solutions displaced from them.

Table No. B.

Freezing point depression of soils near the moisture equivalent. (From Hoagland's data*).

Soil	Moisture Equivalent	Water in sample percent.	Depression O°C	Reference to paper by Hoagland page.	date.
7	13.31	13.6	0.151	380	Oct. 30.
8	8.06	8.2	.122	"	May 7.
9	9.87	9.7	.092	"	Oct. 23.
10	18.38	17.8	.074	384	Oct. 23.
11	16.28	16.3	.052	380	Aug. 21.
12	9.72	9.6	.077	381	May 1.
14	17.99	17.9	.013	"	July 31

* The moisture equivalents are taken from the paper by Burd "Water Extractions of Soils as Criteria of their crop producing Power" J. Ag. Res. XII, No. 6.
The Freezing point depressions from Hoagland's "The Freezing point Method as an Index of Variation in the Soils Solution Due to Season and crop growth." J. Ag. Res. XII, No. 6

BOUYOUCOS' DILATOMETER STUDIES.

The expansion of water on freezing was found by Bunsen to be 0.0907, and by Foote and Saxton (27) 0.0932. The latter workers have computed the water freezing in colloid gels, assuming that the expansion for such water is the same as for water in mass. They recognized the need of experimental proof of this assumption, but thought it was furnished by their experiments with mixtures of lamp black and water which on freezing showed the same expansion as for water alone. From their measurements of the expansion upon freezing of various gels (lamp black, silica, alumina, etc.) they found that a part of the water froze at -6.0°C, or above, and another part at lower temperatures. They called the former "free water", the latter "apparent capillary water", and that which seemed not to freeze at all "combined water". In the case of aluminum oxide they found some capillary water changed to free by repeated freezing, but there was no such change with lamp black.

Bouyoucos (7), who had already concluded that some of the soil water is not free to act as a solvent and probably is unable to freeze, recognized in Foote and Saxton's work an analogy to his problem, and adopted the dilatometer method to use with soils, with the hope of being able to measure the "unfree" water. He divised a new form of dilatometer, which is more convenient for filling than those formerly in use. (See Fig. 3.)

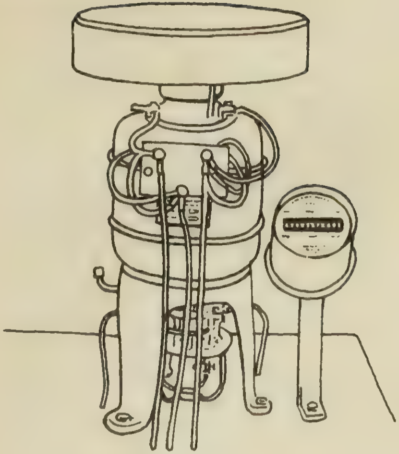

Fig. 1
Centrifuge

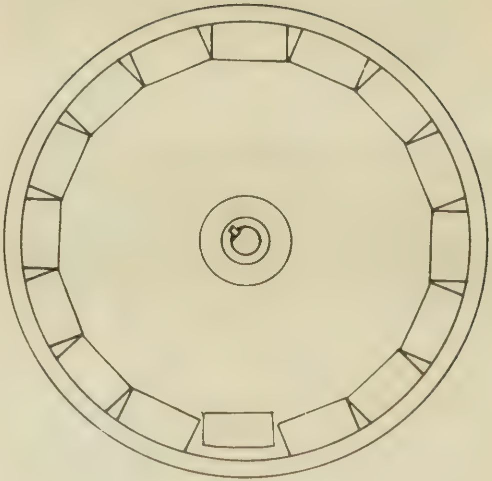

Fig. 2
Cups placed in drum

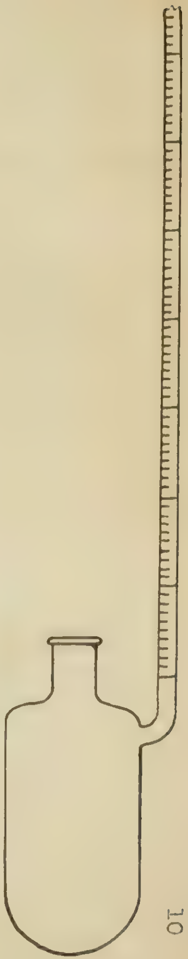

Fig. 3
Dilatometer

Fig. 1.- Centrifugal apparatus for the determining of the moisture equivalent of soil. The soil cups are held in the drum mounted on the motor shaft, and the speed of the motor is shown by the indicator at the side.

Fig. 2.- Showing the interior of the drum and the square soil cups, one displaced to show the fit.

Instrument.

This Bouyoucos' dilatometer is a closed cylinder of glass with rounded top and bottom, with a stoppered opening for filling, and a hollow graduated stem, extended upward from near the top, for reading the expansion.

Method.

The moist sample of soil is weighed and placed in the cylinder, which is then filled with some liquid that is immiscible with water and mobile at low temperature. The dilatometer is closed with a tight stopper, and placed in the freezing bath which has previously been adjusted to the desired temperature (-1.5°C.), and cooled to the temperature of the bath, which must be closely controlled. When the cooling is done, indicated by the coming to rest of the top of the liquid in the stem, the amount of liquid is adjusted so that the top of the liquid column is near the lower end of the graduated portion of the stem, and its position is read and recorded. The freezing is then started by jarring or rubbing the instrument, or by placing it in a still colder bath. If the latter method is employed the dilatometer must be returned to the warmer bath as soon as the freezing begins, which is indicated by a rise of the filling liquid in the stem. Since the instrument and its contents remain at the same temperature as the surrounding bath, no correction needs to be made for change in volume of either soil or filling-liquid, while the expansion of the water in freezing is shown by the volume of filling liquid forced up into the graduated stem. When the column comes to rest, the column is read a second time, and the difference taken as the amount of expansion.

As the amount of water in the moist sample is known and the expansion observed is assumed to be the difference between the volume of the ice and that of the water from which it is formed, the volume of water frozen may be computed from the expansion. Bouyoucos used the factor 10, that is 1 volume expansion indicates 10 volumes of water frozen.

Using this method, Bouyoucos found (7) that part of the water froze near the same temperature as water in mass, a part at lower temperatures, while a part remained unfrozen at the lowest temperatures he could use (-78°C.)- results similar to those obtained by Foote and Saxton with colloidal gels. The readily freezing portion he regarded as identified with his "free water" which he had announced to carry all the soluble matter in the soil solution. The second portion he called capillary-absorbed water, (instead of the "apparent capillary water" of Foote and Saxton), and for the third portion, not freezing at all, he retained Foote and Saxton's term "combined water". He arbitrarily fixed the temperature of -1.5°C as the boundary between the "free" and the "unfree". As he found that most of the "capillary absorbed water" which froze between -1.5° and -78.° would freeze only a few degrees below this upper limit, he placed the lower

limit, for convenience sake, first at -12° and later at -4.0°. The difference in results whether he cooled to -4.0° or to -78.0° was very slight. The temperature limits and in part the nomenclature adopted by Bouyoucos are different from those of Foote and Saxton, although the principles and phenomena discussed are very similar.

He found all three forms of water present in most soils, but their proportions varied widely. He concluded that the unfree water is constant for each soil no matter how great the total amount of water. He observed that repeated freezing and thawing caused an increased expansion, which he interpreted as the changing of some of the unfree water into free, and associated this increased expansion on freezing with the previously mentioned diminished depression of the freezing point observed after repeated freezing and thawing. His dilatometer studies showed that the amount of unfree water was greater for the finer textured soils. He concluded that the combined water was about the same as the maximum amount mentioned above that could be present in a soil that could not be made to freeze, which he had earlier announced is about the same as the wilting coefficient as fixed by Briggs and Schantz, but in later studies concluded there is no close relation, and in still later (9 see P. 20) that the "combined water" is about the same as the hygroscopic coefficient.

Parker (41) alone has attempted to verify Bouyoucos' dilatometer studies of soils. He determined the expansion in the case of a few soils, and apparently accepts the method as showing correctly the amount of water frozen, but attributes the failure of the unfree water to freeze to the pressure of adhesion upon the water films, as he had already shown that such pressure lowers the freezing point. (p. 14).

Bouyoucos, almost from the first, has recognized a vague connection between the fineness of texture of a soil and the depression of its freezing point when wet with a definite amount of water, and similarly between the fineness of texture and the amount of "unfree" water indicated by dilatometer readings. However, previous to Parker's first papers, he reported but few attempts to determine whether any quantitative relation exists between the freezing point depression or the dilatometer expansion and any single-valued expression of soil texture. He had studied the relation between his unfree water and the heat of wetting (9), and established that soils with a high heat of wetting also indicated much "combined" water, and vice-verse, but it is quite clear that he did not consider heat of wetting as a measure of soil texture except in a very general way. In one article only (7) he reported the "unfree" water in six samples of which the moisture equivalent values were furnished him by Dr. Lyman Briggs, but on even these he seems not to have determined the freezing points, and certainly not when brought to the moisture equivalent. He makes no mention of moisture equivalent as a measure of texture, and seems to have regarded the indefinite connection noted as merely incidental to a greater salt content and a greater activity of whatever force caused the water to become unfree, - a force that

he never defined, but seems to regard as more chemical than physical. Soon after Parker's work appeared, Bouyoucos (15) published data comparing the heat of wetting, the moisture equivalent, and the unfree water of 25 soils. He found no constant relation between the moisture equivalent and either of the other values. He critisizes the moisture equivalent method as unreliable, stating that it gives results in some cases higher by 25 percent than the true moisture equivalent, but not indicating how he arrived at that conclusion. In the same article he recognizes that the moisture equivalent is in some degree a measure of soil texture, but points out that colloidal and organic matter are recongized as affecting this value. He states that "at least one more property is coming into play that affects the results appreciably, namely: the activation or nature of the surface". It is not clear what Bouyoucos had in mind in using the term "activation of the surface". In the earlier paper on unfree water and heat of wetting (9) he argued that the heat of wetting is evolved by the water in passing from the liquid state to whatever solid state it (in his opinion) has as combined water, using repeatedly the two terms water of hydration and water of solid solution in describing it. He states that all the energy which is manifested as heat of wetting is furnished by the water, the soil acting merely as a "provocator". In this paper he states "This specific or selective attraction or affinity of the solid materials for water is not due entirely to the magnitude of the surface of the solid materials, but principally to the chemical nature of the materials". There thus seems no doubt that when he used the term "activation" he had in mind some ability to form chemical combinations with water. His data are quoted in table D:

KEEN'S INTERPRETATION AND BOUYOUCOS' REPLY.

Keen (33) taking Bouyoucos' data, made an independent interpretation of these and concluded that, contrary to Bouyoucos' opinion the amount of unfree water varied in the same direction as the total water present. His summary included the following statements."

"(1) The water rendered unfree is not a constant amount, but varies with the total moisture content:

(2) A definite relation exists between the free, unfree and total moisture, expressed by the equations: $Yn = cMn$,

$$An = \frac{1}{\frac{1}{cx}} \cdot Yn^{\frac{1}{x}} - Yn,$$

where c and x are constants for any one soil.

Mn = total moisture content.

Yn = free water.

Zn = unfree water.

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*Keen - Jour. Ag. Science, Vol. 9 - P 414. (1919).

Table D.

RELATIONSHIP FOUND BY BOUYOUCOS BETWEEN HEAT OF WETTING, UNFREE WATER AND MOISTURE EQUIVALENT.

Soil Nos.	Soil Type	Moisture Equivalent Percent	Unfree Water Percent	Heat of Wetting 0°C.
1	Sand	3.8	1.35	0.2
2	Californiz Hardford sandy loam	15.0	5.2	0.8
4	Ohio silt loam	21.3	3.6	0.7
3	Ohio silt loam	21.8	4.6	0.7
8	Rhode Island sandy loam	21.7	6.0	1.1
9	Michigan silt loam	25.5	10.2	1.65
10	Wisconsin Superior clay	28.2	10.75	1.95
6	Pennsylvania	28.9	5.00	0.9
5	Cornell silt loam	29.1	5.25	0.9
7	Pennsylvania silt loam	29.2	7.0	1.1
14	Minnesota Clyde silt loam	29.8	11.0	2.55
12	Michigan clay loam	30.2	13.6	2.2
13	California Willows clay	32.2	12.9	2.2
11	California Capay clay	33.5	11.1	2.0
20	Illinois black clay loam	34.0	14.7	3.5
19	Illinois clay loam	35.8	14.3	3.5
16	Illinois clay loam	36.3	15.2	2.9
15	Minnesota black surface	36.5	14.0	2.85
18	Iowa Carrington clay loam	36.5	16.0	3.4
17	Minnesota Fargo clay	39.0	16.0	3.0
21	California Merced clay	40.2	17.8	4.0
23	Wisconsin black clay loam	46.7	20.9	4.9
22	California Stockton Clay abode	49.5	18.7	4.1
24	Muck	95.5	37.0	8.0
25	Muck	147.0	67.0	12.6

Note. - In this table the samples have been arranged in order of increasing moisture equivalent.

Taken from Bouyoucos Paper Heat of Wetting, Moisture Equivalent and Unfree Water Soil Science XIV, P. 433, (1922).

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(3) The proportion of free to total water continually decreases and that of unfree to total continually increases as the total moisture diminishes in amount, over the experimental range.

(4) The actual amount of free water continually decreases as the total moisture diminishes.

"(5) The same general conclusions on the relations existing between the soil and its moisture content that were drawn from the writer's experiments on the evaporation of water from soil, follow

again. The soil colloids must be considered as primarily concerned in the relations; the soil water present is subjected to the same law over the whole experimental range and the various constant and critical points shown by soil at varying degrees of water contents are approximate equilibrium values only and do not indicate any break or abrupt change in the physical condition of the soil moisture."

In a second paper (34) the same year, Keen considered Bouyoucos' findings in regard to the characteristics of the free and unfree water, and while he regards Bouyoucos' explanation as tentative only, he holds that the results emphasize the need for recognizing that the soil and its water must be considered as a definite system whose parts cannot be considered apart but must be studied as a whole.

Bouyoucos' latest paper (10) dealing with dilatometer measurements, appearing in 1921, is in the nature of a reply to Keen's (33, 34) two papers. He made new determinations on a number of soils and published data which he claimed to show that the unfree water in a soil is the same in amount whether the soil is very wet or comparatively dry. The differences, which he considers slight, he explains by supposing that in the drier portions, some soil particles did not come into contact with the water, and therefore were not wetted and thus could not make any water unfree.

Table E is Bouyoucos' table 1, with a final column added, showing the percentage increase in total unfree water, and in combined water for each soil, comparing the wettest and driest portions. This column does not support Bouyoucos' claim that the results disprove Keen's conclusion.

THE MOISTURE EQUIVALENT.

The moisture equivalent of a soil may be defined as the number of parts of water per hundred parts of dry soil that are retained when the soil is saturated with water and then brought into equilibrium with a centrifugal force of 1000 times gravity. It is an arbitrary value, the determination having been devised by Briggs and McLean (25 and 26) expressly to give a single-valued expression for texture. It always is a desirable supplement to the much more time-consuming mechanical analysis and for some purposes may wholly supplant this. The determination is rapid and replicates are concordant.

Method: The air dry soil, first thoroughly mixed (sifted if necessary) is placed in a square metal moisture cup, with a bottom of fine wire gauze, first covered by a false bottom of filterpaper on which the soil rests. The amount taken, usually about 30 g. for soils of average texture and organic matter content, is such that after the centrifuging the soil will be about 1 cm. deep in the cup. The sample is then saturated by placing the cup in a metal pan, the bottom of which is covered with water so that the lower third of the soil sample is submerged. After about half an hour, by which time the soil will have become thoroughly saturated throughout,

TABLE E

Amount of water rendered unfree by soils at different moisture contents, hygroscopic water not included.

								Increase from driest to wettest %
Coarse Sand								
Moisture content, percent		5.00	7.50	10.00	12.50	15.00	75.00	
Total unfree water	"	1.21	1.52	1.60	1.42	1.51	1.62	34
Combined water	"	0.82	0.68	0.92	0.63	0.84	1.03	25
Medium Fine Sand								
Moisture content	"	5.00	7.50	10.00	12.50	15.00	75.00	
Total unfree water	"	1.84	1.98	1.57	1.83	1.93	2.16	17
Combined water	"	1.25	1.37	1.18	1.45	1.43	1.51	17
Fine Sandy Loam.								
Moisture content	"	7.50	10.00	12.50	15.00	17.50	75.00	
Total unfree water	"	4.24	4.18	4.36	4.52	4.45	4.56	7
Combined water	"	2.43	2.18	2.63	2.34	2.28	2.78	14
Loam								
Moisture content	"		12.50	15.00	17.50	20.00	75.00	
Unfree water	"		8.56	8.17	8.73	8.38	8.82	3
Combined water	"		4.51	4.35	4.16	4.73	4.94	9
Silt loam.								
Moisture content	"		12.50	15.00	17.50	20.00	75.00	
Unfree water	"		9.75	9.35	9.52	9.81	9.84	1
Combined water	"		5.28	5.42	5.37	5.61	5.45	3
Silty Clay Loam.								
Moisture content	"		15.00	17.50	20.00	22.50	75.00	
Unfree water	"		13.62	14.03	13.85	14.04	14.25	5
Combined water	"		7.54	7.61	7.28	7.73	7.92	5
Clay Loam								
Moisture content	"		15.00	17.50	20.00	22.50	75.00	
Unfree water	"		13.13	12.85	12.87	13.24	13.61	4
Combined water	"		7.28	7.42	7.17	7.04	7.58	4
Humus clay loam.								
Moisture content	"		17.50	20.00	22.50	25.00	75.00	
Unfree water	"		15.35	15.82	15.18	15.61	16.34	6
Combined water	"		8.73	8.22	9.05	8.82	9.18	5
Clay								
Moisture content	"		20.00	22.50	25.00	27.50	75.00	
Unfree water	"		14.65	15.18	14.91	15.61	15.45	5
Combined water	"		9.08	9.23	9.35	9.45	9.68	7
Clay								
Moisture content	"		20.00	22.50	25.00	27.50	75.00	
Unfree water	"		15.24	15.46	15.18	15.62	15.85	4
Combined water	"		10.54	10.65	10.56	10.81	11.18	6
Muck								
Moisture content	"		80.00	100.00	120.00	140.00	200.00	
Unfree water	"		63.82	64.15	65.16	64.23	65.28	2
Combined water	"		42.55	42.35	42.91	43.38	44.19	4
Peat								
Moisture content	"		80.00	100.00	120.00	140.00	200.00	
Unfree water	"		69.23	70.15	69.18	70.35	71.13	3
Combines water	"		51.28	51.93	52.18	52.62	53.95	5

Table No. From Bouyoucos: "The Amout of Unfree Water in Soils at Different Moisture Contents". Soil Science Vol. II, P. 258.

the cups are transferred to another pan, the bottom of which is covered with blotting paper, the purpose of which is to remove a part of the water of saturation, the samples, protected from evaporation, are left in this pan for several hours, over night usually, to "temper", so that such a structure will be retained by the sample as to permit the escape of the excess water during the following centrifuging. After the tempering the moisture cups are fitted, bottom outward, into the flat cylindrical drum of the centrifuge, (See Cut, Fig. 2) which accomodates 16 at a time - enough for 8 duplicate samples. The centrifuge is then whirled at 2440 revolutions per minute, which gives a centrifugal force of 1000 times gravity. This speed, which is controlled by an automatic governor, is maintained for 40 minutes, after which the samples are removed and their moisture content determined by drying at 100 to 110°C.

One particular advantage of the method is that the packing of the moist samples is brought about by the uniform centrifugal force acting upon them and is therefore uniform - an important factor and something that can scarcely be accomplished otherwise. The degree of packing is important since it influences not only the total pore-space, but also the number of contacts between soil particles, the diameter of the spaces, and the angles that bound them. Since the values secured by the method are so uniform and comparible, Briggs and his co-workers have developed factors by which other values, such as the hygroscopic coefficient, the so-called wilting point, etc., may be computed from the moisture equivalent, which is much more convenient than determining them directly.

EXPERIMENTAL.

MOISTURE EQUIVALENT.

DETERMINATION

In the case of all the soils dealt with in the following pages the moisture is reported as parts of water per hundred parts of oven-dried soil. (p.p.h.) The moisture equivalent of each was determined in duplicate, according to the method described above (p. 15). The samples of mineral soil were taken in air-dry condition, except in the few cases in which the nature of the particular experiment required oven-dried material. All were passed through a 2 mm. seive, rejecting whatever could not be made to pass through by using a rubber pestle. The peat and leaf mold samples were passed through a 3 mm. seive, and for the moisture equivalent determinations the former were not allowed to become air-dry, but only dry enough to permit of their being passed through the seive.

The concordance of the duplicate determinations of the moisture equivalent may be seen from the data for 98 consecutive samples - 89 mineral soils, 3 leaf molds and 8 peats, (table 1). The greatest divergence between duplicates for any of the 89 mineral soils was 2 p.p.h., the greatest average difference for any one group was 1.1 and the least 0.1. The agreement is closest with the coarser textured soils, and least with the leaf molds and peats, with which there is difficulty in securing duplicates that are really representative, on account of the varying structure and degree of division of the original material, and the necessary exclusion of grinding in preparing the samples. Even with the peats the concordance is fair.

EFFECT OF LEACHING.

Samples of twenty soils from Lac Qui Parle County, Minnesota, were leached with distilled water in the moisture equivalent cups before centrifuging. Each cup with its 30 grams of soil received 750 cc. of water, poured a few cc. at a time upon the surface of the soil, covered with filter paper to protect it from puddling. After this amount of water had been passed through the soil, carrying with it any dissolved matter, the centrifuging, weighting, and drying were done in the usual manner. In every case there was a slight increase in moisture equivalent, this varying from 0.1 to 3.2 p.p.h. with an average of 1.5. Table 2.

The observed increase in the moisture equivalent is in harmony with the findings of Sharp and Waynick (44) who, as a result of moisture equivalent determinations upon soils first treated with salts and then leached, suggested that the removal of salts increases the moisture equivalent.

Table 1 - Concordance of duplicate determinations of moisture equivalent. Part A. Illustrated by data from 90 successive samples.

Part A.

Range in moisture equivalent	Number of Samples	Moisture equivalent			
		Average	Difference between duplicate determinations greatest	least	average
		p.p.h.	p.p.h.	p.p.h.	p.p.h.
Mineral Soils					
1.5 - 2.9	5	1.9	0.1.	0.1.	0.1
3.0 - 3.7	4	3.4	.3	.1	.2
4.7 - 8.7	7	6.3	.5	.1	.2
9.0 - 10.9	9	9.8	1.0	.0	.3
11.8 - 18.4	7	15.4	.6	.0	.2
19.6 - 21.8	7	20.5	1.8	.0	.4
22.6 - 24.8	9	23.6	1.3	.0	.6
25.0 - 26.5	8	25.8	.9	.0	.4
28.0 - 29.0	8	28.4	.9	.0	.4
31.3 - 31.7	6	31.5	.8	.0	.4
34.1 - 35.4	8	34.8	2.0	.3	1.1
37.0 - 38.3	8	37.6	1.8	.2	.8
40.7 - 42.2	3	41.6	1.0	.0	.4
Leaf Molds.					
59.1 - 64.5	3	63.9	3.0	2.0	2.3
Peats					
115.7 - 257.5	8	176.4	5.0	1.0	2.0

Part B. Data on leaf molds and peat soils. Moisture equivalent.

Sample	Determination 1	Determination 2	Average	Difference.
Leaf Molds				
a	62.1	64.1	63.1	2.0
b	63.0	65.0	64.0	2.0
c	66.0	63.0	64.5	3.0
Peat Soils				
d	128.0	131.0	129.5	3.0
e	114.5	117.0	115.7	2.5
f	180.0	181.0	180.5	1.0
g	188.1	185.5	186.7	2.6
h	195.0	192.0	193.5	3.0
i	198.0	201.0	199.5	3.0
j	149.5	146.5	148.0	3.0
k	255.0	260.0	257.5	2.5

The 20 samples in table 2 were selected because of the contrast in freezing point depression, ten of them, group A, showing the greatest and ten, group B, the smallest depression for any of the samples from Lac Qui Parle county. It was expected that leaching would remove more soluble matter from the first ten, and change both freezing point and moisture equivalent more than with the other ten. The change in moisture equivalent, however, is no greater in one set than in the other, the average for each being the same, although the leaching caused much greater changes in freezing point in the case of the former.(p. 40-41. below.)

In another trial the above precaution of leaching in the moisture cups , so as to obviate any need of handling the wet soil with a possible resultant puddling, was not observed. In this, using eight soils from Mille Lacs County, 150-200 gram portions were leached on Bückner funnels after which the saturated soils were transferred to the moisture equivalent cups, using a spoon.

For conparison the same soils were kept covered with water for the same length of time as was required for the leaching, but without allowing it to percolate through them, after which they were transferred to the moisture cups, and the moisture equivalent determined. Table 3. On the average the change is only 0.1 p.p.h. less for the prolonged contact with water without leaching than with the leaching, indicating that the change in moisture equivalent is due more to the action of water than to the removal of salts.

EFFECT OF IGNITION.

A large number of soils were ignited and the moisture equivalent of the ignited residues determined. In every case it was lowered, but data will be presented for only those soils whose residues were used also in the freezing point determination. Table 4.

The decrease in moisture equivalent in a number of cases was about the same as the loss on ignition, but in others much greater and in one (F) much less.

Table 2 - Effect of leaching upon the moisture equivalent

Sample	Moisture equivalent		
	before	after leaching	increase
Group A.			
136	27.8	27.9	0.1
137	28.0	29.8	1.8
140	28.3	30.0	1.7
158	30.1	31.3	1.2
300	30.2	33.4	2.2
174	31.4	33.2	1.8
185	32.5	34.0	1.5
199	35.0	35.1	.1
200	35.3	36.6	1.3
207	36.4	39.6	3.2

Group B Sample	Moisture equivalent before	 after leaching	 increase
49	9.5	10.2	0.7
77	16.0	16.4	.4
84	19.1	21.5	2.4
301	19.6	21.7	2.1
88	19.8	21.0	1.2
98	22.2	23.4	1.2
108	23.9	25.6	1.7
148	29.5	30.5	1.0
151	29.6	31.3	1.7
152	29.7	32.2	2.5

Table 3 - Effect of leaching and of prolonged contact with water upon the moisture equivalent.

Soil	Volume of water used	Number of determinations averaged	Moisture equivalent unleached	leached	Increase	Kept saturated but not leached	Increase due to contact with water
	cc.						
A	1500	4	4.4	4.2	-0.2	4.4	0
B	2000	4	6.0	6.3	.3	7.5	1.5
C	1500	2	11.8	14.9	3.1	13.9	2.1
D	1000	4	12.7	12.8	.1	13.2	.5
E	2000	3	18.9	20.1	1.2	20.1	1.2
F	1500	3	19.6	19.7	.1	20.0	.4
G	750	4	22.1	25.4	3.3	24.3	2.2
H	1500	6	23.5	26.6	3.1	26.1	2.6
Average					1.4		1.3

Table 4 - Change in moisture equivalent brought about by ignition.

Soil	Origin	Loss on ignition	Moisture equivalent before	 after	 decrese	Percentage decrease
		percent				
A	S. New Mexico	1.4	2.8	1.3	1.5	54
B	Western Nebraska	4.0	7.9	3.8	4.1	52
C	Western Nebraska	7.0	13.3	6.3	7.0	53
D	Western Nebraska	5.8	16.5	9.6	6.9	45
E	Western Nebraska	7.3	18.6	10.3	8.3	45
F	E. New Mexico	11.3	20.4	15.8	4.6	23
G	W. Nebraska	8.6	21.5	9.5	12.0	56
H	W. Nebraska	10.0	22.7	12.1	10.6	47
I	Minnesota	7.9	22.8	17.0	5.8	25
J	W. Nebraska	8.0	23.7	9.9	13.8	58
K	S. Arizona	9.4	26.4	14.0	12.4	47
L	E. Nebraska	11.3	26.4	16.7	9.7	37
M	E. Nebraska	9.0	30.8	15.6	15.2	49
N	S. Saskatchewan	19.2	37.0	23.5	15.5	37

RELATION OF FREEZING POINT TO CHANGE IN MOISTURE CONTENT.

The freezing points were determined upon five soils with moisture equivalents ranging from 22.8 to 4.2. Several air dry portions of each were weighed out, the computed amount of water added, and the moistened soil quickly and thoroughly mixed by means of a spatula. The samples were then placed in 1 inch x 8 inch glass test tubes, to be used as freezing point tubes, which were then immediately closed with rubber stoppers and allowed to stand until the next day before making the freezing point determinations.

The data are assembled in table 5. The freezing point depression for each soil increased with increasing dryness of the sample, and did so much more rapidly than the moisture content diminished, thus confirming Bouyoucos' observations.

Table 5 - Freezing point depression of soils at diminishing moisture content.

Soil	Type name	Moisture equivalent	Water per 100 parts dry soil	Depression
			p.p.h.	°C
A	Hempstead silt loam	22.8	24.0	0.124
			21.0	.145
			18.0	.204
			15.0	.307
			12.0	.583
B	Colby silt loam	22.5	30.6	.061
			28.6	.072
			26.6	.089
			18.6	.118
			12.6	.470
			11.6	.808
			11.1	.882
			10.1	1.647
			9.6	2.542
C	Colby silt loam	22.5	22.5	.182
			16.3	.387
			15.3	.485
			14.3	.638
			13.3	.828
D	Fargo fine sandy loam	11.4	20.0	.339
			16.8	.489
			12.8	.662
			11.2	.905
E	Merrimac loamy fine sand	4.2	9.5	.061
			9.1	.072
			8.1	.080
			7.8	.137
			6.0	.172
			4.2	.304

CHANGE IN FREEZING POINT INDUCED BY REPEATED FREEZING AND THAWING.

Using Hempstead silt loam, with a moisture equivalent of 22.8, samples of five different moisture contents were prepared, in the manner previously described, placed in the stoppered freezing point tubes, and these then stored in a small, tight, wooden box with water standing on the bottom, and with sides and top lines with blotting paper which was kept wet, so that the atmosphere about the freezing point tubes was nearly saturated with water vapor. Each sample was frozen four successive times at one or two day intervals, being re-stoppered and returned to this box after each freezing. Table 6.

With four of the five portions there was an appreciable decline in the freezing point depression from one freezing to the next. In one portion (with 15 p.p.h. moisture) there was no definite change.

The cause for this slight change in depression at successive freezings, has been discussed by Bouyoucos, who in his earlier studies attributed it to a change in the amount of "free" water, which in his opinion was increased by the freezing and thawing, and served to dilute the actual soil solution, and in consequence to lessen the freezing point depression. Parker makes no mention of any change in depression due to repeated freezing. Subsequent to Parker's studies Bouyoucos (16) observed that stirring the soil after it had been frozen and thawed, restored the depression to its first magnitude. He explains this observation by saying that the freezing and thawing "removed water from the smaller capillaries in the soil to the larger ones", and that stirring restores the earlier condition.

Table 6 - Depression at successive freezings of the same portions of Hempstead silt loam. (Moisture equvalent = 22.8).

Moisture content	Interval between preparing sample and freezing			
	one day	two days	three days	five days
	°C	°C	°C	°C
24.0	0.184	0.173	0.170	0.150
21.0	.225	.225	.206	.190
18.0	.280	.270	.258	.210
15.0	.381	.405	.386	.390
12,0	.617	.600	,582	.590

AGREEMENT OF DUPLICATE DETERMINATIONS.

The freezing point determinations reported in this table, as well as in tables 5, 7, 8, 9, and 10 are single determinations, The agreement to be expected for duplicate determinations of such samples is shown in Tables 7 Parts A, B, where the individual freezing point depressions for five portions of soil prepared separately in the same manner are given. The maximum range among the five at any one freezing is 0.027°C.

Beginning with table 11 all depressions reported are averages of duplicates, with the exception of those tables where the object is to determine the concordance of duplicates. The concordance is shown and discussed on page 62 and following.

CHANGE IN FREEZING POINT DUE TO CHANGE IN DISTRIBUTION OF MOISTURE.

Comparison was made between the freezing points of soil moistened by the addition of water which was thoroughly mixed with the air dry soil, and those of the same soil when the same amount of water was added to the surface of the sample, but without mixing. That is, although the amount of water was the same the distribution in the first case was made as even and thorough as possible, while in the second the water was only distributed as fast and as thoroughly as gravity and the attraction of the soil for water would bring it about. The data, Table 7, Part A, show that when soil and water are thoroughly mixed together at once, the freezing point changes very little at successive freezings, the average being the same at the fifth freezing as at the first, but for four of the 5 portions prepared at the same time the later depression was slightly the less. The difference at successive freezings of any one portion was not greater than the range in depression at one freezing of the five similar portions.

The results are quite different, however, when to portions of the same soil the same amount of water was simply added to the surface of the sample and not mixed with it. Table 7, Part B. The depression at the first freezing was only slightly more than half as great as when soil and water were mixed, although there had been 24 hours for the water to become distributed through the soil by gravity and capillarity.

Each of the five portions froze with gradually increasing depression at the five successive freezings, and at the last had reached a depression which differed from that of the mixed samples at the same freezing only by an amount that was well within the limit of error.

In a similar set of experiments smaller amounts of water were applied to the surface of the samples in the freezing point tubes and allowed to stand without stirring. Table 8. The results, like those in the second part of the preceding table, show a comparatively small depression at the first freezing, and increasing depression at the successive freezings, as the water become more thoroughly distributed throughout the soil. A point of interest is that the increase in depression at successive freezings is greatest with the driest samples. This effect upon the freezing point of the progressive moistening of the soil is explained by the following considerations as to what takes place when a soil is moistened by simply adding water to the surface of the air-dry sample and leaving it undisturbed.

Table 7. - Depression at successive freezings of the same portions of Hempstead silt loam moistened with amounts of water required to bring to moisture equivalent (22.8).

Part A. Soil and water thoroughly mixed.

Portion	Time after moistening	Depression at successive freezing. 1 day	3 days	5 days	8 days	10 days	Moisture found
		°C	°C	°C	°C	°C	p.p.h.
1		0.078	.080	.075	0.85	.070	22.8
2		.080	.072	.075	.082	.076	23.5
3		.078	.087	.085	.087	.088	22.6
4		.073	.075	.080	.078	.068	22.2
5		.081	.060	.065	.082	.065	22.7
Average		.078	.077	.076	.083	.078	22.6
Range		.008	.027	.020	.011	.023	

Part B. Water simply added to surface of soil in the freezing point tube, without stirring.

Portion	Time after moistening	1 day	3 days	5 days	8 days	10 days	Moisture found
1		0.043	.052	.059	.066	.073	22.8
2		.037	.052	.055	.085	.083	22.8
3		.042	.040	.050	.077	.080	22.8
4		.050	.060	.064	.070	.080	22.8
5		.047	.060	.065	.067	.073	22.8
Average		.044	.053	.059	.073	.076	22.8
Range		.013	.020	.015	.019	.010	

Table 8 - Depression at successive freezings of the same portions of Hempstead silt loam when moistened with various amounts of water, but not mixed to hasten distribution.

Portion	Interval after moistening	Depression at successive freezings 2 days	5 days	8 days	Moisture found
		°C	°C	°C	p.p.h.
1		0.057	.056	.062	21.6
2		.052	.062	.083	19.6
3		.069	.112	.143	17.5
4		.114	.212	lost	15.5
5		.175	.282	.338	13.4
6		.265	.572	.643	11.3

A part or all of the surface becomes saturated, and a zone below partially saturated, while the portion at the bottom may still be as dry as it was before any water was added. With the lapse of time the water gradually moves from the surface toward the drier bottom soil, with zones of intermediate moistness between. If the amount of water is not too great, there comes a time when the surface is no longer saturated, and if it is not too little, when all of the soil is moistened, although it may be a long time before top and bottom become equally moist. If the amount of added water is small, months at least would pass before the moisture would become uniformly distributed. Another series of progressive zones will at the same time exist in respect to the soluble matter of the soil, which on account of the thorough mixing of the samples is uniformly distributed before the water is added. The zone at the top of the sample will be moistened with least concentrated solution, and the lowest moistened zone of the soil will be bathed by most concentrated solution, partly as a consequence of the greater amount of water at the top, and partly due to the leaching effect of the advancing water.

If we now consider the effects of the situation just described we see that the tendency will be for the observed freezing point to be the actual freezing point of that part of the soil that freezes at the highest temperature, viz; the wettest. In the case described it will be the portion of the soil nearest the surface. If the soil is allowed to than and after some time frozen again, the observed freezing point should become lower with each freezing, until the movement of both water and soluble matter has practically ceased, for the reason that the surface zone is becoming drier by loss of water to the lower zones, and as the solution in it is becoming more concentrated by the upward diffusion of soluble matter. Even then, provided the amount of added water is so small that top and bottom of the soil have not become equally moist when the water practically ceases to move, the depression will be less than if the same amount of water were uniformly distributed through the soil.

The data in table 7, part B, indicate that when water enough had been added to bring the soil to the moisture equivalent, the static condition was not reached until after eight days had elapsed, when the depression was found to be practically the same as for the mixed samples reported in the first part of the same table. In the drier portions reported in table 8 some doubtless had not reached that static condition.

This slow distribution suggests that even when soil and added water are well mixed, and the water thus only has short distances to move, the particles may not all be equally wet unless the proportion of water is high.

FREEZING POINTS OF SOILS WITH AN ARBITRARY AMOUNT OF WATER.

In nearly all of his work Bouyoucos prepared his samples for freezing by adding a definite amount of water to the air dry soil, very frequently 20 per cent.

Twenty four samples of three soil-types from Rice County, Minnesota, were prepared in this way, mixing the water with the air dry soil thoroughly but quickly, then storing over night in tightly covered tin boxes before the freezing. On the following day the samples were frozen to determine the depression, and then dried in an oven to determine the amount of water actually present, which of course, was more than 20 parts per hundred of dry soil. This excess is due to the hygroscopic moisture present in the air dry soils before mixing with the added water. Since the finer textured soils contained more of this hygroscopic moisture, they also contained more total water when frozen. This total amount of water present, considered as a percentage of the moisture equivalent, is here termed the relative wetness of the soil in table 9.

In the table the data are arranged in order of relative wetness. In general the freezing point depression increases as relative wetness decreases, but there are striking exceptions as with soils E, O, and T. These irregularities may be due to considerable differences in the salt content of the soils, but probably in part to the irregular distribution of the water upon the soil particles even though soil and added water had been well mixed.

Table 9. - Effect of relative wetness of soils on their freezing points.

Sample	Relative wetness water / Moisture equivalent	Moisture content	Moisture equivalent	Depression.
	Group I			
	per cent	p.p.h.		°C
A	128	21.7	16.9	0.186
B	100	20.6	20.6	.110
C	99	21.7	21.9	.108
D	94	19.2	20.5	.088
E	93	20.9	22.6	.190
F	92	20.2	22.0	.100
Average	101	20.7	20.8	.130
	Group II			
G	88	21.7	24.8	.180
H	85	20.6	24.4	.223
I	84	20.2	24.1	.129
J	83	20.9	25.1	.174
K	81	22.4	27.7	.240
L	80	20.5	25.5	.265
Average	83	21.0	35.3	.202

Table 9 Cont.

Sample	Relative wetness water / Moisture equivalent	Moisture content	Moisture Equivalent	Depression
Group III				
M	79	24.1	30.3	.580
N	78	23.4	30.1	.359
O	78	21.8	28.1	.158
P	77	22.6	29.6	.337
Q	76	22.8	30.1	.247
R	74	21.9	29.5	.465
Average	77	22.8	29.6	.357
Group IV.				
S	73	18.8	25.9	.867
T	73	22.2	30.6	.306
U	72	23.6	38.8	.594
V	67	24.9	37.2	.741
W	66	23.9	35.9	.470
X	63	28.7	45.9	1.595
Average	69	23.7	35.7	.760

FREEZING POINT DEPRESSION WHEN AIR DRY SOILS ARE BROUGHT TO MOISTURE EQUIVALENT BY ADDITION OF COMPUTED AMOUNTS OF WATER.

Each of thirteen air dry soils of known moisture content, was thoroughly mixed with the amount of water necessary to bring it to its moisture equivalent, then stored in the closed freezing point tubes over night and frozen. The same soils were also frozen in the same way with three-fourths and half of these amounts of water, and also when brought to the moisture equivalent by centrifuging the saturated soils. Five of the soils could not be frozen in the driest condition. The object was to determine (Table 10) the depression for each soil at the same three degrees of relative wetness, 100, 75, and 50 percent, produced by adding the computed amount of water, and also at 100 when this was secured by centrifuging the saturated soil.

Considering first the depressions of the samples moistened by mixing soil and water, the depression varies at the moisture equivalent from .068° to .528°, at three-fourths the moisture equivalent, from .182 to 1.076°, and at half the moisture equivalent, from .678 to 1.358.

There is no regularity shown in the rate of increase of the depression with increasing dryness, although in every case there is a marked increase. Of the five soils that failed to freeze at 50 percent wetness only one showed very great depressions at 100 percent and only two at 75 percent. The uniformity of depression at each degree of wetness is too slight to indicate a constant. The extremely variable results may be due to differences in salt concentration, or to incomplete distribution of the water in the soil mass.

Table 10 - Freezing point depressions of soils moistened to the moisture equivalent by centrifuging and to definite fractions of that moisture content by adding water without centrifuging.

Soil Source.	Moisture equivalent	Freezing point depression Centrifuged	:Water added and mixed into soil.		
Fraction of moisture equivalent		1.00	1.00	0.75	0.50
		°C	°C	°C	°C
		-	-	-	-
B Western Nebraska	6.7	.343	.398	.758	1.108
C " "	13.3	.111	.153	.353	- -
D " "	15.9	.054	.116	.195	- -
E " "	18.6	.157	.180	.467	- -
F E. New Mexico	18.7	.279	.528	1.076	- -
G Western Nebraska	19.6	.068	.152	.232	1.032
H " "	22.1	.064	.118	.187	.782
I Minnesota	22.8	.075	.076	.583	.920
J Western Nebraska	22.8	.078	.126	.182	.978
K S. Arizona	26.0	.092	.108	.251	1.358
L Eastern Nebraska	25.6	.097	.172	.264	1.064
M " "	29.2	.125	.152	.264	1.092
N S. Saskatchewan	37.5	.114	.203	.320	.678

The depression for the samples brought to the moisture equivalent by first saturating the soil with water and then centrifuging, exactly as is done in the ordinary determination of the moisture equivalent, was less with each soil than for the sample equally wet without centrifuging; and on the whole was less variable. The difference is to be attributed to the loss of soluble matter in the water centrifuged away.

FREEZING POINT DEPRESSION OF SOILS BROUGHT TO THE MOISTURE EQUIVALENT BY CENTRIFUGING SATURATED SAMPLES.

The freezing point depression of 268 Minnesota soils, covering a great range in texture, was determined by the Bouyoucos method, after the soil samples had been brought to the moisture equivalent by centrifuging, as described above (p.15).

The duplicate samples of soil, each at just the moisture equivalent, were removed from the cups, thoroughly but quickly mixed, and duplicate portions transferred to the glass freezing point tubes for the freezing point determination, in the manner Bouyoucos advised, while two other portions were placed in tared aluminum boxes to be dried at 100°-110°C in order to determine the moisture content, and thereby the moisture equivalent.

There are several advantages in this method of bringing the soil to the moisture equivalent rather than by the method of mixing with the computed amount of water. 1. The simplicity of procedure and certainty of bringing the sample to just the moisture equivalent. 2. The even distribution of the water throughout the soil. 3. The small amount of handling to which the sample is subjected with consequent lessening of risk of evaporation of water.

The most serious disadvantage of this method of preparing the sample for freezing is, that the soil is wetted to saturation, the maximum water capacity, and any soluble matter present is distributed through this larger volume of water. As this excess of water is thrown off in the later centrifuging it takes with it a part of the dissolved material. Accordingly, while the soil is moistened evenly and just to the desired degree, the moistening solution is more dilute than when the computed amount of water is added without centrifuging. In consequence the freezing point depression will be less. Such centrifuged samples should be expected to show a depression more nearly constant as well as smaller than that of soils brought to the same moisture content without centrifuging.

In reporting the data Table 11, the samples are arranged in order of moisture equivalent. In order to bring out any general relation that may exist between moisture equivalent and freezing point depression the data from the 268 samples have been averaged in 19 groups. Table 12.

The freezing point depressions reported in this table are the averages of duplicates, the concordance of which are shown and discussed in a later section (p.62).

The greatest depression occurs with samples of very low moisture equivalent, the average for the nine samples with moisture equivalent below 3.0 p.p.h. being 0.271°C. For the groups with moisture equivalent of 3.0 or above, the average depression ranges from 0.035° to 0.099°C, with no evident relation to the moisture equivalent. The great depression found for the soils of very low moisture equivalent is probably due to the difficulty of determining the true freezing point (as suggested by Fisher. See 28. Footnote on page 362.) because too little heat is released to warm the system to the true freezing point of the soil.* The slow rate of heat evolution may also have a bearing.

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* Bouyoucos (20-P-9) mentioned the possibility that in some comparatively dry soils the proper freezing point may not be observed because too little water is frozen to warm the mass to its true freezing point, but his reference to it is so brief and so obscure that it is not certain that he considered that this condition might exist even if all the water (unfree as well as "free") could be frozen. He was discussed the amount of only "free" water, and seems to have had in mind the failure to observe any freezing at all, rather than the recording of an incorrect freezing point.

[illegible]

[illegible] Solid chromium [illegible] oxidizing 10, but the [illegible]

[illegible]

[illegible] solution (p. 7).

[illegible] 0.2700. The [illegible]

[illegible]

Table 11 - Freezing point depression of Minnesota soils brought to the moisture equivalent by centrifuging - determined by Bouyoucos method.

Reference number	Moisture equivalent	Depression °C	Depth of Section Inches	Source County	Laboratory number.
1	1.5	0.452	61-72	Aitkin	16168
2	1.6	.310	61-72	"	16169
3	1.7	.240	25-36	"	16279
4	1.7	.446	25-36	"	16166
5	1.7	.188	37-48	"	16167
6	1.9	.118	25-36	"	16273
7	2.6	.330	25-36	"	16289
8	2.9	.190	13-24	"	16278
9	2.9	.167	13-24	"	16165
10	3.0	.092	25-36	"	16189
11	3.3	.074	25-24	"	16188
12	3.7	.057	25-36	"	16202
13	3.7	.052	25-36	"	16194
14	3.7	.072	37-48	"	16195
15	4.0	.078	13-24	"	16201
16	4.0	.088	13-24	"	16272
17	4.1	.049	37-24	"	16203
18	4.2	.062	49-60	"	16204
19	4.3	.082	6-36	"	16293
20	4.5	.120	6-12	"	16277
21	4.6	.070	61-72	"	16205
22	4.7	.069	49-60	"	16196
23	4.8	.106	61-72	"	16213
23	5.1	.039	13-24	"	16193
25	5.4	.051	6-12	"	16200
26	5.9	.043	61-72	"	16197
27	5.9	.059	6-12	"	16271
28	6.0	.064	13-24	"	16178
29	6.0	.077	25-36	"	16179
30	6.3	.049	6-12	"	16187
31	6.4	.062	49-60	"	16212
32	6.5	.052	1-6	"	16270
33	6.5	.085	2-6	"	16276
34	6.7	.047	37-48	"	16227
35	7.2	.042	25-36	"	16226
36	7.2	.058	49-60	"	16228
37	7.4	.044	1-3	"	16198
38	7.4	.032	13-24	"	16183
39	7.9	.030	6-12	"	16232
40	8.5	.058	1-6	"	16191
41	8.6	.047	13-24	"	16209
42	8.7	.071	6-12	"	16192
43	8.8	.048	1-2	"	16275
44	8.9	.042	6-12	"	16182
45	8.9	.034	16-36	"	16283

Table 11 Continued

Reference Number	Moisture equivalent	Depression	Depth of Section	Source County	Laboratory number
		°C	inches		
46	9.0	.042	1-6	"	16186
47	9.3	.098	-1	Lac Qui Parle	15155
48	9.4	.026	25-36	Aitkin	16174
49	9.5	.042	1	Lac Qui Parle	15156
50	9.5	.057	1	" " "	15157
51	9.5	.059	1	" " "	15154
52	9.6	.038	1-2	Aitkin	16291
53	9.8	.060	37-48	"	16211
54	10.1	.059	2-6	"	16292
55	10.3	.045	6-12	"	16177
56	10.4	.042	1-6	"	16181
57	10.6	.037	6.12	"	16208
58	10.9	.025	25-36	"	16173
59	11.8	.033	25-36	"	16184
60	12.0	.041	13-24	"	16233
61	12.0	.028	5.19	"	16287
62	12.4	.035	1.6	"	16231
63	12.6	.050	25-36	"	16210
64	12.6	.042	25-36	"	16234
65	12.8	.029	1-6	"	16176
66	12.8	.022	3-19	"	16266
67	13.2	.040	19-23	"	16288
68	13.7	.054	1-6	"	16207
69	13.9	.039	2-16	"	16282
70	14.1	.031	6-12	"	16172
71	14.3	.037	½-3	"	16265
72	14.5	.034	3-5	"	16286
73	15.0	.049	1	Lac Qui Parle	15147
74	15.0	.050	1-3	Aitkin	16285
75	15.8	.085	13-24	"	16225
76	16.0	.042	1	Lac Qui Parle	15149
77	16.0	.055	1	" " "	15146
78	16.0	.035	1-2	Aitkin	16281
79	16.3	.037	22-72	"	16268
80	16.6	.064	61-72	"	16229
81	17.0	.032	1-6	"	16171
82	18.1	.056	1	Lac Qui Parle	15144
83	18.4	.043	25-36	Rice	7963
84	19.1	.034	1	Lac Qui Parle	15150
85	18.6	.048	1	" " "	15135
86	19.7	.044	25-36	Rice	7971
87	19.7	.026	19-22	Aitkin	16267
88	19.8	.045	1	Lac Qui Parle	15148
89	20.8	.044	6-12	Rice	7965
90	20.8	.054	25-36	"	7967
91	21.2	.038	13-24	Jackson	15553
92	21.2	.054	13-24	Rice	7966
93	21.8	.049	1	Lac Qui Parle	15137
94	21.9	.051	1-6	Jackson	15538

Table 11 Continued

Reference Number	Moisture equivalent	Depression	Depth of Section	Source County	Laboratory number
		°C	inches		
95	22.0	.100	25-36	Nobles	5672
96	22.1	.038	leaf mold	Aitkin	16198
97	22.1	.035	1	Lac Qui Parle	15151
98	22.1	.040	1	" " "	15152
99	22.2	.042	1	" " "	15153
100	22.6	.099	1-6	Aitkin	16306
101	22.6	.046	6-12	Rice	7961
102	22.7	.046	1-12	Fillmore	5643
103	22.8	.044	25-36	Rice	7969
104	22.9	.047	leaf mold	Aitkin	16269
105	23.1	.053	13-24	Houston	5641
106	23.2	.048	13-24	Rice	7970
107	23.4	.140	25-36	Jackson	15554
108	23.9	.044	1	Lac Qui Parle	15134
109	24.0	.050	13-24	Rice	7962
110	24.0	.069	1-6	Rice	7964
111	24.2	.068	1-12	Houston	5640
112	24.3	.055	25-36	Rice	7947
113	24.3	.055	1-6	Rice	7968
114	24.4	.051	25-36	Fillmore	5645
115	24.5	.041	1-6	Rice	7960
116	24.6	.059	1	Lac Qui Parle	15140
117	24.6	.234	25-36	Nobles	5669
118	24.8	.098	13-24	"	5671
119	24.9	.052	25-36	Houston	5642
120	25.0	.055	1	Lac Qui Parle	15141
121	25.1	.045	13-24	Fillmore	5644
122	25.5	.046	25-36	Rice	7955
123	25.6	.049	1	Lac Qui Parle	15138
124	25.8	.059	1	" " "	15142
125	25.9	.055	1	" " "	15145
126	25.9	.059	13-24	Rice	7950
127	25.9	.072	1-12	Nobles	5670
128	26.0	.061	25-36	Rice	7951
129	26.2	.074	25-36	Rock	5675
130	26.3	.049	1	Lac Qui Parle	-15136
131	26.5	.061	25-36	" " "	14962
132	26.6	.062	61-72	" " "	14996
133	27.0	.053	13-24	" " "	14961
134	27.0	.116	49-60	" " "	14971
135	27.1	.092	61-72	" " "	14972
136	27.8	.133	37-48	" " "	14970
137	28.0	.300	25-36	" " "	14989
138	28.2	.065	6-12	Rice	7949
139	28.2	.051	1	Lac Qui Parle	15103
140	28.3	.127	25-36	" " "	14985
141	28.5	.059	1	" " "	15124
142	28.7	.055	1	" " "	15152
143	28.7	.066	13-24	" " "	14992

Table 11 Continued

Reference Number	Moisture Equivalent	Depression	Depth of Section	Source County	Laboratory number
		°C	Inches		
144	29.0	.060	7-12	Lac Qui Parle	14960
145	29.0	.063	37-48	" " "	14963
146	29.3	.028	37-48	Aitkin	16235
147	29.4	.068	6-12	Rice	7945
148	29.5	.047	37-48	Lac Qui Parle	14956
149	29.5	.069	1-6	Rice	7948
150	29.5	.068	13-24	Rice	7954
151	29.6	.046	13-24	Lac Qui Parle	14954
152	29.7	.046	13-24	" " "	14979
153	29.7	.065	1-6	" " "	14959
154	29.7	.085	13-24	Rock	5674
155	29.9	.083	1	Lac Qui Parle	15133
156	30.1	.079	7-12	Jackson	15552
157	30.1	.068	1	Lac Qui Parle	15108
158	30.1	.141	13-24	" " "	14984
159	30.2	.073	49-60	" " "	14964
160	30.2	.096	1	"" " "	15128
161	30.4	.053	7-12	" " "	14953
162	30.5	.073	1-6	Rice	7944
163	30.6	.071	0-6	Lac Qui Parle	14952
164	30.7	.068	7-12	" " "	14991
165	30.8	.050	49-36	" " "	14957
166	30.8	.065	1-6	" " "	14966
167	30.8	.103	25-36	" " "	14976
168	30.8	.090	13-24	Rice	7958
169	31.0	.068	1	Lac Qui Parle	15143
170	31.1	.064	7-12	" " "	14967
171	31.3	.061	61-72	" " "	14965
172	31.4	.050	61-72	" " "	14958
173	31.4	.065	49-60	" " "	14995
174	31.4	.243	13-24	" " "	14988
175	31.7	.060	1	" " "	15139
176	31.7	.084	37-48	" " "	14994
177	31.9	.049	25-36	" " "	14955
178	31.9	.065	25-36	" " "	14980
179	32.2	.056	1	" " "	15104
180	32.2	.056	1	" " "	15120
181	32.4	.066	1	" " "	15126
182	32.4	.105	25-36	Rice	7959
183	32.5	.063	1	Lac Qui Parle	15122
184	32.5	.079	7-12	Rice	7957
185	32.6	.145	7-12	Lac Qui Parle	14983
186	32.8	.124	13-24	" " "	14975
187	33.1	.064	1	" " "	15109
188	33.1	.087	1	" " "	14993
189	33.4	.066	1	" " "	15110
190	33.4	.102	37-48	" " "	14981
191	33.5	.111	7-12	Jackson	15556
192	33.6	.066	1	Lac Qui Parle	15106

Table 11 Continued

Reference Number	Moisture equivalent	Depression °C	Depth in Section Inches	Source County	Laboratory number
193	33.8	.048	1-6	Lac Qui Parle	14977
194	33.9	.050	1	" " "	15119
195	34.1	.074	1	" " ""	15112
196	34.1	.104	1	" " "	15113
197	34.2	.063	1	" " "	15105
198	34.8	.063	1-6	"" " "	14990
199	35.0	.160	7-12	" " "	14987
200	35.3	.145	1-6	" " "	14982
201	35.3	.102	1-6	Rice	7956
202	35.4	.053	1	Lac Qui Parle	15121
203	35.6	.073	1-6	" " "	14986
204	36.1	.075	7-12	Rice	7953
205	36.3	.054	7-12	Lac Qui Parle	14978
206	36.4	.064	25-36	" " "	14948
207	36.4	.140	1-6	" " ""	14997
208	36.5	.068	1-6	Rice	7608
209	36.7	.093	1	Lac Qui Parle	15132
210	36.8	.130	1	" " "	15127
211	36.8	.130	7-12	Jackson	15540
212	37.0	.067	7-12	Lac Qui Parle	14946
213	37.0	.117	7-12	" " "	14974
214	37.1	.057	1	" " "	15125
215	37.3	.055	1	" " "	15118
216	37.9	.083	1	" " "	15129
217	38.0	.063	1-6	Rice	7604
218	38.0	.108	13-24	" " "	14947
219	38.3	.057	1	" " "	15107
220	38.6	.079	1	" " "	15114
221	38.7	.093	1	" " "	15130
222	38.7	.055	1	" " "	15123
223	38.8	.068	1	" " "	15111
224	39.3	.065	37-48	" " "	14949
225	39.7	.067	1	" " "	15116
226	39.9	.109	1-6	" " "	14975
227	40.7	.090	49-60	" " "	14950
228	40.7	.117	1-6	Rice	7595
229	40.8	.122	1-6	Jackson	15555
230	41.2	.062	1-6	Rice	7626
231	41.3	.078	49-60	Lac Qui Parle	14945
232	41.8	.092	1-6	Rice	7599
233	42.2	.127	61-72	Lac Qui Parle	14951
234	42.6	.103	1	" " "	15131
235	43.6	.078	1-6	Rice	7586
236	43.8	.112	1	Lac Qui Parle	15117
237	44.0	.061	1-6	Rice	7952
238	45.3	.092	1-6	"	7622
239	45.4	.077	1-6	"	7590
240	45.7	.089	1	Lac Qui Parle	15115
241	45.9	.130	1-6	Jackson	15856

Table 11 Continued

Reference Number	Moisture equivalent	Depression °C	Depth in Section Inches	Source County	Laboratory number
242	46.8	.095	1-6	Rice	7617
243	46.9	.052	leaf mold	Aitkin	16175
244	47.2	.062	1-6	Rice	7613
245	49.9	.136	25-36	Jackson	15598
246	57.3	.075	1-6	"	15838
247	58.0	.127	13-24	"	15597
248	58.1	.096	7-12	"	15588
249	60.9	.075	1-6	"	15591
250	63.1	.053	leaf mold	Aitkin	16170
251	63.4	.121	1-6	Jackson	15852
252	64.0	.026	leaf mold	Aitkin	16185
253	64.4	.037	" "	"	16190
254	64.5	.030	" "	"	16206
255	69.8	.100	7-12	Jackson	15596
256	72.1	.105	7-12	"	15853
257	75.1	.086	7-12	"	15855
258	77.3	.041	leaf mold	Aitkin	16294
259	78.4	.061	1-6 muck	Jackson	15840
260	86.0	.061	1-6	"	15854
261	97.0	.097	leaf mold	Aitkin	16230
262	103.7	.055	" "	"	16280
263	115.0	.052	" "	"	16274
264	129.5	.042	" "	"	16180
265	180.5	.037	Peat 1-6	Mille Lacs	Peat 3
266	186.7	.046	" 1-6	" "	Peat 2
267	193.5	.059	" 1-6	" "	Peat 1
268	199.5	.032	" 1-6	" "	Peat 4

Table 12 - Extreme and average freezing point depression of Minnesota soils grouped by moisture equivalent.

Moisture Equivalent	Number of samples	Depression for group greatest °C	least °C	Average depression °C	
1.5- 2.9	9	0.452	0.118	0.271	mineral soils
3.0- 4.9	14	.120	.049	.078	" "
5.0- 6.9	11	.085	.039	.057	" "
7.0- 8.9	11	.071	.030	.046	" "
9.0-10.9	13	.098	.025	.047	" "
11.0-12.9	8	.050	.022	.035	" "
13.0-15.9	9	.085	.031	.046	" "
16.0-18.9	8	.064	.032	.046	" "
19.0-21.9	11	.054	.026	.044	" "
22.0-24.9	25	.234	.035	.066	" "
25.0-27.9	17	.133	.045	.067	" "
28.0-30.9	32	.300	.028	..077	" "
31.0-33.9	26	.243	.048	.081	" "
34.0-36.9	17	.160	.053	.094	" "

Table 12 continued

Moisture equivalent	Number of Samples	Depression for group greatest	least	Average depression	
		°C	°C	°C	
37.0-39.9	15	.117	.055	.076	mineral soils
40.0-45.9	15	.130	.061	.87	" "
46.0-69.9	14	.136	.026	.077)	muck soils
70.0-99.9	6	.105	.041	.069)	muck soils
10.0-20.0	7	.055	.032	.046	peat soils
Average of all	268	-	-	.075	

Let us consider the case (somewhat different from that given by Fisher) in which we have a sample of 25 g. soil with 1.5 p.p.h., or .375 g. of water. If, when this is supercooled by 2°C, and then frozen rather slowly, all the water should be frozen, 30 calories will be released to warm the system by two degrees. The known heat requirement may be placed rather roughly as follows:

Ice 0.375 g. to be warmed 2°C, requires .	0.4 cal.
Soil, 25 g. " " " (about) .	10.0 cal.
Glass freezing point tube ($\frac{1}{2}$ being near the sample)	8.0 cal.
Thermometer, perhaps	2.0 cal.
Total	20.4 cal.

If two thirds of the water were frozen instantly instead of slowly, only enough heat would be released to warm the system to the freezing point, while if the supercooling was 3 degrees, not enough heat would be released to warm the system to the freezing point even if there was no escape of heat to the surrounding cooling chamber. Experience shows that the freezing is not instantaneous but gradual. The loss of heat by radiation to the cooling chamber is thus a factor, as the slower the freezing the greater will be the time during which heat may be lost. The fact that those samples frozen with little water remain at the maximum temperature only a very short time, was observed. This confirms the observation of Bouyoucos, who, however, obscured his statement of this observation (19. P. 12) by referring to concentration of the solution as the explanation.

The short duration of time at the maximum height of the mercury suggests that the maximum temperature observed is not the true freezing point, but only the meeting point of a rise due to released heat, and a fall due to radiation. These considerations make it doubtful whether the true freezing point of these coarser textured soils is really lower than the more uniform freezing points for the finer textured ones.

EFFECT OF PROLONGED SATURATION OF SOIL WITH WATER, AND OF LEACHING, UPON THE FREEZING POINTS OF SOILS BROUGHT TO THE MOISTURE EQUIVALENT BY CENTRIFUGING.

In order to determine the effect of prolonged contact of soil with water, and of removal of the soluble matter, upon the freezing points of soils brought to the moisture equivalent by centrifuging, eight soils were frozen by the Bouyoucos method after being subjected to these treatments. The soils which range in moisture equivalent from 4.4 to 23.5, were prepared in three different ways for the centrifuging as described above (P. 20-22).

The freezing point depressions are given in table 13. On the average the leaching reduced the depression markedly, (from .095°C. to .052°), but the prolonged saturation without leaching had only a slight effect, reducing the depression only from .095° to .088°.

Considering the average depressions for each soil separately, the first statement holds true for 5 of the soils, while for two (H and D) of the other three the difference is moderate. The second statement holds true in the case of five of the eight as well. The effect of leaching is not distinctly greater with the soils of higher moisture equivalent, the greatest change being found in the case of soil C. with a moisture equivalent of 11.8.

There is a tendency for the greatest change to be found in the case of samples showing the greatest depression in the unleached condition. The order of magnitude of this depression for the samples prepared in the usual way is C A B F G E D H and for the leached portions is C A F G B D H E. Of the eight soils two are in the same position in both lists, four have changed their positions by one place each, and the remaining two by only two places.

EFFECT UPON FREEZING POINT OF VERY THOROUGH LEACHING OF SOILS LATER BROUGHT TO MOISTURE EQUIVALENT.

In order more fully to determine the effect of leaching upon the freezing point depressions, twenty Lac Qui Parle samples reported in Table 11 were selected and a new determination of freezing point for each made after thorough leaching with distilled water. The samples form two groups of ten each, the one, A, comprising the ten Lac Qui Parle samples that showed the greatest freezing point depression, and the other, B, the ten that showed smallest depression.

In order to avoid having to transfer the wetted soil to the moisture cups after the leaching, which might have an influence upon the values, the leaching in this series of determinations was performed after the air dry soil had been placed in the centrifuge cups, instead of in funnels as had been done in the series just above reported.

[illegible]

[illegible]

[illegible] of the amount [illegible] The sole [illegible]

[illegible]

[illegible] was distributed [illegible] the greatest [illegible] could [illegible] equivalent of 1/4.

[illegible] necessary for the [illegible] change [illegible]

[illegible]

[illegible]

[illegible]

Table 13 - Freezing point depression of Minnesota soils first long saturated or leached and then brought to the moisture equivalent by centrifuging.

Determination	soil description	Moisture equivalent	Freezing point depression sample - how prepared after usual method	 after prolonged saturation	 after thorough leaching	Duration of saturation or of leaching	Volume of leaching
		p.p.h.	°C	°C	°C	days	cc.
1	A 1-6 in. section of		0.157	.140	.102	1	1500
2	Merrimac loamy sand		.177	.182	.126	3	1500
3			.144	.141	.083	5	1500
4			--	.095	.072	26	1500
Average		4.4	.159	.140	.096		
1	B 1-12 in. section of		.093	.083	.089	2	2000
2	red sandy loam		.142	.173	.067	6	3600
3			--	.140	.098	8	2000
4			--	.104	.109	15	2000
Average		6.0	.118	.125	.091		
1	C 1-12 in. section of		.176	.172	.043	16	1500
2	Fargo fine sandy loam				.040	--	1500
Average		11.8	.176	.172	.041		
1	D 49-60 in. section		.027	.021	.043	4	1000
2	red fine sandy loam		.067	.038	.027	2	1000
3			--	..004	.016	9	1000
4			--	.019	.027	4	1000
Average		12.7	.047	.021	.028		
1	E 1-12 in. section of		.058	.076	.059	3	2000
2	red loam		.045	.047	.043	7	2000
3			.046	.031	.036	9	2000
Average		18.9	.050	.051	.046		
1	F 84-96 in. section of		.100	.083	.071	2	1000
2	red silt loam		.099	.093	.053	2	2000
3			.089	.081	.050	4	1000
4			--	.055	.045	6	2000
Average		19.6	.096	.078	.055		
1	G 25-36 in. section of		.065	.095	.038	4	500
2	red silt loam		.101	.091	.075	2	1500
3			.076	.059	.020	3	500
4			.083	.082	.052	4	1500
Average		22.1	.081	.082	.048		
1	H 1-6 in. section of		--	.015	.034	10	1500
2	Hempstead silt loam		.043	.037	.028	2	1500
3			.043	.010	.010	4	1500
4			.029	.036	.040	3	1500
5			.051	.041	.046	2	1500
6			--	.081	.024	24	1500
Average		23.5	.042	.037	.029		
Average of all determinations			.095	.088	.052		

After the soils had been placed in the cups, just as they would be for the moisture equivalent determination, instead of placing the filled cups in a pan of water, the distilled water was poured upon the soils in the cups, and allowed to leach through, the surface of the soil in each cup being first covered with a square of filter paper to protect it from mechanical puddling, and the water added in small portions. When from 1500 to 3000 cc. of water had leached through each of the cups, which contained about 30 g. of soil, the samples were centrifuged as described above and the freezing points determined.

Of the twenty soils thus treated, all but one show a smaller depression after the leaching Table 14 and with this one the change was less than the experimental error. The average for the ten of greatest depression fell from 0.166°C to.056°C, while the average for the other ten fell only from .042° to .032. The change for individual soils ranges from .082 to .247°C in the A group, with an average of .110; and from -.001° to .018 C in the B group, with an average of .010°. The percentage of change, based upon the depression of the unleached sample, varies in group A from 54.3% to 82.3%, but in group B varies only from -3% to 40.5%. It is very evident that with these comparatively uniform soils, leaching causes greater change in freezing point in the samples showing greatest depression in the unleached condition.

Table 14 - Change in freezing point depression brought about by leaching of Lac Qui Parle County soils. Determined by Bouyoucos' method.

Reference-Number	Moisture equivalent	Depression of unleached portion	Depression of leached portion	Change decrease	Change decrease percentage
	p.p.h.	°C.	°C.	°C.	
A					
137	28.0	0.300	0.053	0.247	82.3
174	31.4	.243	.057	.186	76.1
199	35.0	.160	.072	.088	55.0
200	35.3	.145	.064	.081	55.8
185	32.6	.145	.062	.083	57.2
158	30.1	.141	.054	.087	61.7
207	36.1	.140	.064	.076	54.3
136	27.8	.133	.051	.082	61.7
300	30.2	.130	.045	.085	65.4
140	28.3	.127	.040	.087	68.5
Average	-	.166	.056	.110	66.3

Table 14 continued

Reference Number	Moisture equivalent	Depression of unleached portion	Depression of leached portion	Change decrease	Change decrease percentage
	p.p.h.	oC	oC	oC	
B					
301	21.6	.048	.036	.012	25.0
148	29.5	.047	.034	.013	27.7
152	29.7	.046	.028	.018	39.1
88	19.8	.045	.035	.010	22.2
108	23.9	.044	.031	.013	29.3
77	16.0	.042	.025	.017	40.5
49	9.5	.042	.040	.002	4.7
98	22.1	.040	.027	.013	32.2
84	19.1	.034	.033	.001	3.0
151	29.6	.033	.034	-.001	-3.0
Average	-	.042	.032	.010	23.8

Table 15 - Change in freezing point depression brought about by ignition of soil.

Soil	Source	Loss on ignition	Moisture equivalent before ignition	Moisture equivalent after ignition	Freezing point depression before ignition	Freezing point depression after ignition	Change in depression increase	Change in depression decrease
		per cent	p.p.h.	p.p.h.	oC	oC	oC	oC
A	Southern N. Mexico	1.4	2.8	1.3	0.142	0.203	.061	
B	Western Nebraska	4.0	7.9	3.8	.100	.134	.034	
C	"	7.0	13.3	6.3	.111	.187	.076	
D	"	5.8	16.5	9.6	.054	.071	.017	
E	"	7.3	18.6	10.3	.116	.180	.064	
F	E. New Mexico	11.3	20.4	15.8	.279	.163		.116
G	Western Nebraska	8.6	21.6	9.5	.068	.053		.015
H	" "	10.0	22.7	12.1	.064	.178	.114	
I	Minnesota	7.9	22.8	17.0	.090	.081		.009
J	Western Nebraska	8.0	23.7	9.9	.078	.054		.024
K	S. Arizona	9.4	26.4	14.0	.092	.085		.007
L	E. Nebraska	11.3	26.4	16.7	.097	.080		.017
M	" "	9.0	30.8	15.6	.125	.094		.031
N	S. Saskatchewan	19.2	37.0	23.5	.114	.185	.071	
Average					.109	.125	.062	.031

The explanation for the change brought about by the leaching is that it removed soluble matter, so that the solution remaining was less concentrated and therefore froze with less depression. The greater change in depression shown by group A is due to the greater amount of soluble matter they carried, which was removed by leaching.

EFFECT OF IGNITION UPON FREEZING POINT OF SOILS.

Samples of the 14 mineral soils dealt with in table 4 were ignited in the muffle furnace and frozen after being brought to the moisture equivalent by centrifuging in the manner above described.

It has been shown above P. 22 that with all these soils, the ignition lowered the moisture equivalent, the amount of this change varying from 1.5 p.p.h. to 15.2 p.p.h., the former being 54 and the latter being 49 per cent of the moisture equivalent for the unignited soils

With the freezing point depression there was no regularity, seven samples showing an increase averaging .062°C, and seven a decrease averaging .031°C. Table 15.

The greater number of the increases occurred with the coarser textured soils - those of smaller moisture equivalent, although the soil of highest moisture equivalent in the list also showed an increase in depression due to ignition.

If the difference in freezing point depression of materials frozen at the moisture equivalent is due entirely to differences in concentration of the solutions wetting them, as Parker suggested, it would not be expected that the change due to ignition should be in the same direction for all soils, since the ignition may expel some soluble matter already present, and also produce new, the character of the soil determining the amount of each. Thus, the final amount in the soil may be either more or less than the soil originally contained.

The results tend to confirm, rather than to disprove, Bouyoucos' observation that ignited samples show less depression than the unignited when both are frozen with the same amount of water, this tendency being due to the fact that the moisture equivalent is always less in the ignited portion, and so with an arbitrary amount of added water this portion will be relatively wetter. On the whole, the results support Parker's view of the depression being due both to the concentration of the solution and to the force holding it to the particles.

ESTIMATED FREEZING POINT OF SOILS FROZEN WITH 20 PERCENT OF WATER ADDED TO THE AIR DRY SOIL.

Soils moistened with 20 percent of water added to the air dry soil, as Bouyoucos frequently prepared soils for freezing, may be either wetter or drier than the moisture equivalent, depending on the moisture equivalent and the amount of hygroscopic water in the air-dry soil. The latter varies considerably with the conditions of storage and humidity of the air, but may be estimated with some degree of accuracy from the moisture equivalent, as Alway and Clark (2) showed that samples in equilibrium with the same air have the same ratio between hygroscopic moisture and hygroscopic coefficient and Briggs and Shantz showed that a rather constant ratio exists between hygroscopic coefficient and moisture equivalent. If then the ratio between moisture equivalent and hygroscopic moisture be established for a few soils in equilibrium with the air under the same conditions, the ratio may be used to compute the hygroscopic moisture from the moisture equivalent of other soils at equilibrium under the same conditions.

The moisture present in samples of 14 soils of known moisture equivalent was determined, and the ratio between the two values computed with results as follows:

Sample	Ratio percent.
A	14.0
B	8.3
C	13.1
D	20.0
E	13.0
F	11.8
G	14.7
H	19.2
I	15.0
J	20.2
K	9.4
L	13.7
M	13.8
N	17.0
Average	14.6

The ratio is not constant and probably indicates that some of the samples were not in equilibrium with the surrounding air, but the average probably represents something similar to the average condition of samples called "air-dry".

Using this factor (for convenience taken as 15-100), the hygroscopic moisture has been computed from the moisture equivalent for the 3 samples nearest the center of each group in table 11. Table 16.

The total water present in each sample when moistened by the addition of 20 percent of water has also been computed, and from that and the moisture equivalents, the ratios between these values.

The computed depression of freezing point is found by division of that observed at moisture equivalent, by the ratio of total moisture to moisture equivalent. We may take for illustration, sample 35.

Moisture equivalent given = 7.2
" " x 0.15 = 1.1 p.p.h. hygroscopic moisture with 100 grams dry soil, 1.1 grams hygroscopic moisture + 20% water = 20.22 p.p.h. water added.
1.1 + 20.22 = 21.3 p.p.h. total water present.
21.3 ÷ 7.2 -= 2.96 ratio $\frac{\text{total water}}{\text{moisture equivalent.}}$
depression at moisture equivalent 0.042°c ÷ 2.96 ratio = .014°c computed depression.

The depression at moisture equivalent varies irregularly, from .030°C to .446°, the latter in the case of the very coarse soils which has already been mentioned as probably abnormal because too little water is present to be frozen.

The depression computed as described, varies from .010°C to .244°C., the latter maximum depression not with the coarse soils as in the case when frozen at moisture equivalent, but in the case of the finer soils, as Bouyoucos observed.

The soils of low moisture equivalent all (with the exception of the abnormal ones mentioned) have very slight computed depression while all the samples of high moisture equivalent have greater depressions, though they are not greater than found for some samples at the moisture equivalent. The difference in the computed depression between soils of high and low moisture equivalent would no doubt be still greater except for the smaller depressions due to the loss of soluble matter in the water which is carried away in the centrifuging.

Table 16 - Freezing point depression of air dry soils + 20 % added water, estimated from that of the same samples frozen when moistened to the moisture equivalent.

Reference Number	Moisture equivalent	Hygroscopic water (.15 x moisture equivalent)	Total moisture hygroscopic + 20 per cent	ratio total water / moisture equivalent	Depression at moisture equivalent	Estimated depression of soil with 20% of added water
		p.p.h.	p.p.h		°C	°C
4	1.7	.2	20.2	11.9	.446	0.038
5	1.7	.2	20.2	11.9	.188	.016
6	1.9	.3	20.3	11.9	.118	.010
16	4.0	.6	20.7	5.2	.088	.017
17	4.1	.6	20.7	5.0	.049	.010
18	4.2	.6	20.7	4.9	.062	.013
28	6.0	.9	21.1	3.52	.064	.018
29	6.0	.9	21.1	3.52	.077	.022
30	6.3	.9	21.1	3.35	.049	.017
39	7.9	1.2	21.4	2.84	.030	.011
40	8.5	1.3	21.5	2.53	.058	.023
41	8.6	1.3	21.5	2.50	.047	.019
51	9.5	1.4	21.7	2.28	.059	.026
52	9.6	1.4	21.7	2.26	.038	.017
53	9.8	1.5	21.8	2.22	.060	.027
62	12.4	1.9	22.3	1.80	.035	.019
63	12.6	1.9	22.3	1.77	.050	.028
64	12.6	1.9	22.3	1.77	.052	.029
70	14.1	2.1	22.5	1.60	.031	.019
71	14.3	2.1	22.5	1.57	.037	.024
72	14.5	2.2	22.6	1.56	.034	.022

Table 16 Continued

Reference Number	Moisture equivalent	Hygroscopic water (.15 x moisture equivalent	Total moisture hygroscopic + 20 per cent	Ratio total water / moisture equivalent	Depression at moisture equivalent	Estimated depression of soil with 20% of added water
%		p.p.h.	p.p.h.		°C	°C
78	16.0	2.4	22.9	1.43	.035	.024
79	16.3	2.4	22.9	1.40	.037	.026
80	16.6	2.5	23.0	1.39	.064	.046
88	19.8	3.0	23.6	1.19	.045	.038
89	20.8	3.1	23.7	1.14	.044	.039
90	20.8	3.1	23.7	1.14	.054	.047
105	23.1	3.5	24.2	1.05	.053	.051
106	23.2	3.5	24.2	1.04	.048	.046
107	23.4	3.5	24.2	1.03	.140	.136
127	25.9	3.9	24.7	.95	.072	.076
128	26.0	3.9	24.7	.95	.061	.064
129	26.2	3.9	24.7	.94	.074	.079
152	29.7	4.4	25.3	.85	.065	.077
153	29.7	4.4	25.3	.85	.085	.100
154	29.7	4.4	25.3	.85	.083	.098
179	32.2	4.8	25.8	.80	.056	.070
180	32.2	4.8	25.8	.80	.056	.070
181	32.4	4.9	25.9	.80	.066	.082
202	35.4	5.3	26.4	.75	.053	.071
203	35.6	5.3	26.4	.74	.073	.098
204	36.1	5.4	26.5	.73	.075	.103
218	38.0	5.7	26.8	.71	.108	.152
219	38.3	5.7	26.8	.70	.057	.082
220	38.6	5.8	27.0	.70	.079	.113
233	42.2	6.3	27.6	.66	.127	.193
234	42.6	6.4	27.7	.65	.103	.159
235	43.6	6.5	27.8	.64	.078	.122
247	58.0	8.7	30.4	.52	.127	.244
248	58.1	8.7	30.4	.52	.096	.185
249	60.9	9.1	30.9	.51	.075	.147
257	75.1	11.2	33.4	.44	.086	.196
258	77.3	11.6	33.9	.44	.041	.093
259	78.4	11.8	34.2	.44	.061	.138

EFFECTS UPON THE FREEZING POINT OF THE MANNER OF PACKING OF THE SOIL SAMPLES IN THE FREEZING POINT TUBE.

After the completion of the freezing point determinations reported above there appeared an article by Fisher (28) "The Freezing of Water in capillary systems: A critical study", which deals with the expansion of water upon freezing. This suggested to the writer the importance of a very carefulyconsideration of the influence upon the freezing point exerted by variations in the manner and degree of packing of the sample into the freezing point tube, something to which no previous investigators have alluded.

Fisher's paper, which reported no experimental data, deals with the change in volume on freezing of the water that is held in annular-wedge-form between soil particles, but does not deal with its freezing temperature. He argued that, due to surface tension, a given amount of water in such wedges occupies a greater volume than it would as water in bulk, and in consequence upon freezing to ice of normal density the increase in volume is less than for water in bulk. He specifically agreed with Parker that the freezing point of moist soil is influenced by the force (pressure) exerted upon the convex water films, causing their freezing-point to be depressed. It would follow, although Fisher does not so state, that the freezing point of the expanded wedge-water would be raised above that of water in bulk. All investigators in this field, however, have found that the freezing points of moist soils are invariably below that of water in bulk, even when salts have been reduced in amount by leaching, which at first seems to discredit Fisher's view.

A careful consideration, however, may remove this apparent contradiction. While the freezing point of such wedge water may be above that of water in bulk, the freezing will not be transmitted from one wedge to another until the film connecting them is frozen, and the film, being compressed, has a lower freezing point. Thus, the observed freezing point for the moist sample will be that of the films, even though the true freezing point of the wedges, comprising the greater amount of the water, is higher.

A consideration of the effect upon the thickness of the films, of packing a moistered, but not saturated sample suggests two possible conditions, viz:

1: Increased packing may increase the number of points of contact between the soil particles, each with its annular wedge of water to be secured at the expense of the films. The latter will thus become thinner, and in consequence the freezing point will fall.

2: The soil particles near enough to one another to hold wedges of water between them may be forced still closer by the packing, so that the wedges without increase in volume may cover more of the surface of the soil particles, thus requiring the films to cover less

and so allowing them to become thicker, with a resultant rise in the freezing point. Whether Fisher's view of the density of wedge water is or is not fully accepted, it seems certain that change in the thickness of the water films should be accompanied by a change in the freezing point of the moist soil sample, the amount of which might be perceptible.

Both effects probably follow the packing of every sample, and only experimental determination will decide which has the more marked influence upon the freezing point. In the first trial of packing the sample about the bulb of the thermometer, using a stirring rod for the purpose, it was found that a smaller freezing point depression was observed, and further, that this effect was heightened by packing the sample more tightly. This observation led to further trials, which showed that with peat soils, wet exactly to the moisture equivalent, the observed depression could, by very tight packing, be brought down to zero, or even to a minus value, that is to say, one which indicated that the peat froze above 0°C. It was recognized that this result could not be wholly due to the packing's effect upon the true freezing point. The probable explanation is that the somewhat plastic moist packed soil pressed upon the thin walled bulb of the Beckman thermometer, deforming it, and forcing some of the mercury upward into the tube, with a consequent unduly high reading. Proof that the thin walled bulb actually yields to pressure is readily given by packing the soil rather snugly about the bulb in the freezing point tube, and then observing the sudden rise of the mercury in the column when a small stirring rod is thrust into the soil beside the bulb. In many cases the fall of the column when the rod is removed is even more convincing, since the rise might be thought to indicate rapid warming of the mercury due to friction. Of course the soil and stirring rod should be at the same temperature to avoid the mere transfer of heat. It thus came about that instead of only the above mentioned uninvestigated possible cause of difference there is as well the one just mentioned, the compression of the thermometer bulb, a source of positive error, the frequency and magnitude of which in the work previously done it was desirable to estimate if possible.

In freezing point determinations of moist soils this deformation or compression of the thermometer-bulb by the moist soil sample is a most insidious source of error, which later was found to have effected many of the determinations reported above. It must be prevented if correct freezing point determinations are to be secured. No other workers have mentioned it, although Bouyoucos (19 P. 13) approached it when, in his first article, he considered the possibility that the moist soil in freezing might expand so as to press upon the bulb and force mercury up into the tube. He considered that this error from expansion of the freezing soil could occur only when the moist soil was extremely compacted, and that a sufficient precaution was taken in "moving the thermometer in the soil beforehand", before the freezing (see 19 Page 13). This statement is somewhat ambiguous, but has been interpreted by the writer to mean a rotation of the thermometer.

This brief statement by Bouyoucos was noted, and the precaution he advised (interpreted as stated above), has been observed in all the freezing point determinations made in this laboratory, but this precaution is not sufficient to insure against compression by the somewhat unyielding moist soil, as will be shown later.

Bouyoucos did not discuss the more common and more important pressure upon the bulb not due to expansion of the freezing soil, but to failure of the moist sample to yield freely when the thermometer is introduced. The condition is intensified if the sample is further packed after the thermometer is in place. To guard against this the writer has in the determinations reported below used a packing instrument made from a straight glass rod smoothly rounded, or of a tube closed and rounded by heating. The rod which must be slightly larger (about 1 mm) in diameter than the thermometer bulb, is pressed into the moist soil sample in the bottom of the freezing point tube, using first a smaller rod if necessary. The soil is packed tightly or loosely about it with a smaller rod, after which the larger is withdrawn with a rotating motion so as to leave molded in the sample a smooth cylinderical hollow with round bottom into which the thermometer bulb fits easily with only a slight air space about it, and with no danger of compression either before or during the freezing.

Using this means to avoid compression of the bulb, and packing the sample tightly for comparison with similar samples left loose or very slightly packed, it was easy to show that the packing, although unstandardized and not uniform in degree, has a marked effect upon the freezing point.

EFFECT OF DEGREE OF COMPACTNESS UPON FREEZING POINT DEPRESSION.

Eighty two samples, first brought to the moisture equivalent by centrifuging, were frozen, both tightly packed into place as above described, and in as loose a condition as could be well secured Table 17. In 27 of these the depression was greater in the tightly packed condition, the average difference being 0.043°C, in 53 depression was less, the average difference being 0.019°C, while in the two remaining samples there was no difference.

It was observed that often the samples frozen in the loose condition were very slow in coming to the maximum temperature, which is taken as the freezing point, a fact which tends to make such determinations unsatisfactory, as the longer time gives greater chance for loss of heat by radiation and consequent failure to warm to the true freezing point of the sample. It thus appears that compactness of the sample has a decided influence upon the freezing point, and oftener than otherwise the more compact sample freezes with less depression; but the number of cases in which the difference is in the opposite direction is so great, and the magnitude of the difference is so variable, that neither direction nor amount can be predicted for any particular sample.

[illegible]

[illegible] of the same [illegible] is [illegible]

[illegible] the [illegible] of [illegible]

[illegible] Very difficult, [illegible] the [illegible]

[illegible]

[illegible]

[illegible]

Bouyoucos' practice (see 19, page 16) was to freeze the samples in a "slightly compacted" state, rather than loose, and as no other investigator mentions this subject it is probable that all have followed his practice. It is to be supposed that the degree of compactness will have an effect upon the extent of change in freezing point brought about, and possible in direction of change as well, but since no degree of compactness has been agreed upon as most desirable, and there is as yet no nomenclature used to express differences in degree, it is unlikely that any two workers have used the same degree of compactness, or even that any one has consistently used the same degree throughout his own work.

It may be that the degree of compactness which exists in the moisture cups at the end of the centrifuging in the moisutre equivalent determination might be a desirable one, and readily attainable, but there may be difficulty in preserving that degree of compactness until the freezing is performed.

Table 17 - Effect of packing of moist soil samples upon freezing points.

Reference Number	Moisture equivalent	Depression of Freezing point with soil		Change induced by packing		Laborator number
		loose	tightly packed	increase	decrease	
		oC	oC	oC	oC	
3	1.7	.230	.240	.010		16279
6	1.9	.181	.118		.063	16273
A	2.4	.365	.294		.071	14
8	2.9	.244	.190		.054	16278
12	3.7	.067	.057		.010	16202
15	4.0	.087	.078		.009	16201
16	4.0	.104	.088		.016	16272
17	4.1	.064	.049		.015	16203
18	4.2	.069	.062		.007	16204
293	4.4	.118	.095		.023	16297
21	4.6	.088	.070		.018	16205
294	4.7	.151	.134		.017	16296
295	4.8	.063	.056		.007	16304
25	5.4	.070	.051		.019	16200
26	5.9	.072	.043		.029	16197
27	5.9	.085	.043		.042	16271
296	6.3	.075	.058		.017	16308
32	6.5	.079	.052		.027	16270
33	6.5	.108	.085		.023	16276
B	6.7	.165	.167	.002		
37	7.4	.070	.044		.026	16198
297	8.2	.039	.051	.012		16302
298	8.4	.077	.044		.033	16295
43	8.8	.080	.048		.032	16275
45	8.9	.040	.034		.006	16283

Reference Number	Moisture equivalent	Depression of Freezing point with soil		Change induced by packing		Laboratory number
		loose	tightly packed	increase	depcrease	
		oC	oC	oC	oC	
299	9.6	.045	.032		.013	16301
53	9.9	.027	.029	.002		16311
61	12.0	.037	.028		.009	16287
269	12.6	.086	.055		.031	16303
66	12.8	.037	.022		.015	16266
C	13.3	.105	.111		.006	
271	13.6	.038	.034		.004	16310
69	13.9	.035	.030		.005	16282
71	14.3	.052	.037		.015	16265
72	14.5	.045	.034		.011	16286
74	15.0	.050	.050	.000	.000	
272	15.0	.048	.037		.011	16300
D	15.9	.080	.114	.034		
78	16.0	.041	.035		.006	16281
79	16.3	.056	.037		.019	16268
E	18.6	.090	.116	.026		
F	18.7	.285	.390	.105		
G	19.6	.102	.080		.022	
86	19.7	.041	.026		.015	16267
273	19.7	.059	.068	.009		5656
274	20.8	.084	.164	.080		5663
275	21.5	.149	.122		.027	5662
276	21.9	.086	.115	.029		5667
100	22.6	.220	.099	.121		16306
J	22.8	.070	.118	.048		
104	22.9	.040	.047	.007		16269
277	24.3	.100	.150	.050		5661
278	24.5	.200	.290	.090		5666
279	24.6	.160	.234	.074		5669
L	25.6	.108	.124	.016		
280	26.1	.265	.337	.072		5665
281	26.5	.220	.253	.033		5668
282	27.2	.135	.163	.028		5660
284	29.7	.147	.193	.046		5659
M	28.5	.130	.152	.022		
285	30.3	.130	.220	.090		5664
195	34.1	.085	.081		.004	15112
196	34.1	.092	.083		.009	15113
286	36.7	.103	.150	.047		5658
N	37.5	.120	.216	.096		
220	38.6	.170	.119		.051	15114
225	38.8	.095	.080		.015	15116
236	43.8	.115	.132	.017		15117
240	45.7	.125	.110		.015	15115
287	65.8	.066	.056		.010	16299
288	77.3	.048	.041		.007	16294
289	77.5	.040	.038		.002	16309

Table 17 Continued

Reference Number	Moisture equivalent	Depression of freezing point with soil		Change induced by packing		Laboratory number
		loose	tightly packed	Increase	decrease	
290	81.8	.054	.041		.013	16290
291	83.4	.052	.041		.011	16284
292	96.5	.061	.051		.010	16305
262	104.0	.066	.055		.011	16280
263	115.0	.052	.052	.000	.000	16274
267	195.0	.070	.043		.027	Peat 1
266	175.0	.068	.030		.038	" 2
265	180.0	.067	.062		.005	" 3
268	200.0	.066	.076	.010		" 4
269	104.0	.047	.041		.006	" 5

EFFECT OF COMPRESSION OF THE THERMOMETER-BULB

A comparison of the freezing point depression of samples packed into place before introducing the thermometer with that of the same samples when the soil was packed about the thermometer bulb so as to press upon the latter is shown in Table 18. The samples at both freezings were probably compacted to about the same degree, so that most of the difference is to be attributed to the compression of the thermometer bulb. Of the 36 samples Table 18 frozen under both conditions for this comparision, 32 showed a higher freezing point when the thermometer was introduced before the packing, the difference varying from 0.001° to .117°, with an average of 0.030°, a very large error when compared with the average observed depression of .075° found for 268 samples reported in Table (11). In the case of the four samples that showed change in the opposite direction, the difference in two was too small to be significant.

Since the effect of any compression of the thermometer bulb is always to show a freezing point higher than the correct one, it is evident that increased degree of packing and compression of the bulb (when not guarded against) will not only usually occur together), but will usually change the result in the same direction. The two items are thus closely related in laboratory practice.

Since Bouyoucos was the first to publish methods for freezing point determinations of soils, and no later workers have mentioned any modification of his methods, in this respect, it is presumed that all the data hitherto reported have been taken with only the precautions he suggested and are probably all subject to the error here pointed out.

Table 18 - Effect upon freezing point depression depending upon whether sample is packed about the thermometer, or packed before introduction of the thermometer.

Reference Number	Moisture equivalent	Freezing point depression: soil Packed		Change produced by compression of thermometer bulb.		Laboratory Number
		Before	After	Increase	Decrease	
		°C	°C	°C	°C	
A	2.4	.294	.343	.049		
293	4.4	.095	.088		.007	16297
294	4.7	.134	.111		.023	16297
295	4.8	.056	.053		.003	16304
296	6.3	.058	.055		.003	16308
B	6.7	.167	.130		.037	
298	8.4	.044	.001		.043	16295
299	9.6	.032	.027		.005	16301
53	9.9	.029	.016		.013	16311
270	13.3	.111	.090		.021	16298
C	13.0	.034	.027		.007	
271	13.6	.034	.027		.007	16310
272	15.0	.037	.039	.002		16300
D	15.9	.114	.044		.070	
E	18.6	.116	.067		.049	
F	18.7	.390	.273		.037	
G	19.6	.080	.058		.022	
100	22.6	.099	.070		.029	16306
J	22.8	.118	.055		.063	
104	22.9	.047	.026		.021	16269
L	25.6	.124	.100		.024	
283	27.5	.139	.115		.024	16307
M	28.5	.152	.113		.039	
195	34.1	.081	.050		.031	15112
196	34.1	.033	.055		.028	15113
N	37.5	.216	.245	.029		
220	38.6	.119	.088		.031	15114
225	38.8	.080	.050		.030	15116
X	39.7	.089	.058		.031	
236	43.8	.132	.105		.027	15117
240	45.7	.110	.067		.043	15115
Peat 267	195.0	.043	-.015		.058	1
" 266	173.0	.030	.031	.001		2
" 265	180.0	.062	-.011		.074	3
" 268	280.0	.076	.030		.046	4
" 269	104.0	.044	.025		.019	5

MODIFIED METHOD FOR DETERMINATION OF FREEZING POINT.

Because of the considerations above mentioned, the writer has adopted the following procedure to be followed in determining freezing points of soils previously determined by Bouyoucos' method.

The sample is placed in the freezing point tube just as it comes from the moisture equivalent centrifuge, and packed firmly above the rod as described above, so as to mold a properly formed hollow to receive the thermometer bulb, which is then inserted in place of the rod, and the freezing point determination made.

162 of the samples that had been frozen before the effects of packing of the soil and of the compression of the thermometer bulb had been recognized, using only the precautions advised by Bouyoucos, were later frozen by the modified method above described. 142 of them were also frozen after packing the soil about the thermometer bulb so as to bring about the compression. See Tables 19, 20.

Table 19 shows that for 150 samples the depression was less when Bouyoucos' precautions were observed than when the soil was packed and molded into place before the thermometer was introduced, and was greater in only 12 samples. The average difference for the 150 samples was 0.039°C. and for the 12 was .015°C. Of this 12, 3, with much greater difference than the average, occurred with samples of very low moisture equivalent where, as earlier pointed out, the readings are rather untrustworthy because of the possible lack of sufficient heat released in freezing the small amount of water present to warm the system to its true freezing point. It appears that in more than nine-tenths of the freezing point determinations made with only the precaution advised by Bouyoucos, there is a greater or less degree of error due to compression of the thermometer, and that its average magnitude is considerable. The average depression for the whole series frozen with Bouyoucos' precautions was .077°, and for those packed before introducing the thermometer was .113°, an average difference of .036°.

Table 19 - Freezing point depressions by Bouyoucos' method compared with those of the same samples packed into place before introduction of the thermometer.

Reference Number	Moisture equivalent	Depression: Bouyoucos' procedure	Depression: Packed into place	Difference due to packing into place: Increase	Difference due to packing into place: Decrease	Difference between duplicates: Bouyoucos' procedure	Difference between duplicates: Packed into place	Laboratory Number
		°C	°C	°C	°C	°C	°C	
1	1.5	0.452	.441		.011	.005	.022	16168
2	1.7	.310	.271		.039	.014	.022	16169
4	1.7	.446	.381		.065	.048	.016	16166
5	1.7	.188	.264	.076		.020	.028	16167
9	2.9	.167	.179	.012		.020	.022	16165
10	3.0	.092	.189	.097		.001	.012	16189
11	3.3	.074	.095	.021		.004	.016	16188
13	3.7	.052	.114	.062		.019	.017	16194
14	3.7	.072	.090	.018		.000	.005	16195
22	4.7	.069	.076	.007		--	.005	16196
24	5.1	.039	.096	.057		.001	.005	16193
28	6.0	.064	.077	.013		.005	.007	16178
29	6.0	.077	.075		.002	.011	.007	16179
30	6.3	.049	.078	.029		.006	.014	16187
38	7.4	.032	.093	.061		.003	.006	16183
42	8.7	.071	.077	.006		.008	.006	16192
44	8.9	.042	.093	.051		.003	.023	16182
46	9.0	.042	.096	.054		.003	.012	16186
47	9.3	.098	.111	.013		--	.013	15155
48	9.4	.026	.074	.048		.010	.013	16174
49	9.5	.042	.081	.039		.012	.003	15156
50	9.5	.057	.081	.024		.009	--	15157
51	9.5	.059	.105	.046		.026	.004	15154
55	10.3	.045	.057	.012		.005	.010	16177
56	10.4	.042	.071	.029		.010	.004	16181
58	10.9	.025	.050	.025		.005	.007	16173
59	11.8	.033	.093	.060		.003	.010	16184
65	12.8	.029	.098	.069		.003	.008	16176
70	14.1	.031	.036	.005		.004	.010	16172
76	16.0	.042	.071	.029		.003	.005	15149
81	17.0	.032	.051	.019		.006	.010	16171
82	18.1	.056	.070	.014		.008	.004	15144
83	18.4	.043	.105	.062		.002	.005	7963
85	19.6	.048	.060	.012		.008	.006	15135
86	19.7	.044	.096	.052		.004	.007	7971
88	19.8	.045	.075	.030		.002	.008	15148
89	20.8	.044	.094	.050		.008	.008	7965
90	20.8	.054	.136	.082		.005	.005	7967
92	21.2	.054	.110	.056		.004	.004	7966
93	21.8	.049	.069	.020		.021	.017	15137

Table 19 Continued

Reference Number	Moisture equivalent	Depression: Bouyoucos procedure	Depression: packed into place	Difference due to packing into place: Increase	Difference due to packing into place: decrease	Difference between duplicates: Bouyoucos procedure	Difference between duplicates: Packed into place	Laboratory Number
		°C	°C	°C	°C	°C	°C	
97	22.1	.035	.073	.038		.010	.011	15151
98	22.1	.040	.069	.029		.004	.011	15152
99	22.2	.042	.062	.020		.004	.010	15153
101	22.6	.046	.086	.042		.003	.011	7961
103	22.8	.044	.079	.035		.000	.002	7969
106	23.2	.048	.093	.045		.005	.010	7970
107	23.9	.044	.075	.031		.009	.005	15134
109	24.0	.050	.100	.050		.001	.006	7962
110	24.0	.069	.101	.032		.008	.006	7964
113	24.3	.055	.084	.029		.001	.008	7968
115	24.5	.041	.083	.042		.004	.010	7960
116	24.6	.059	.072	.013		.000	.004	15140
120	25.0	.055	.051		.004	.003	.002	15141
122	25.5	.046	.087	.041		.013	.004	7955
123	25.6	.049	.074	.025		.017	.002	15138
124	25.8	.059	.084	.025		.012	.008	15142
126	25.9	.059	.115	.056		.002	.004	7950
128	26.0	.061	.147	.086		.004	.015	7951
130	26.3	.049	.071	.022		.001	.007	15136
131	26.5	.061	.135	.074		.019	.014	14962
132	26.6	.062	.084	.022		.008	.009	14996
133	27.0	.053	.137	.084		.001	.023	14961
134	27.0	.116	.168	.052		.013	.010	14971
135	27.1	.092	.139	.047		.004	.007	14972
136	27.8	.133	.200	.067		.014	.004	14970
137	28.0	.300	.306	.006		.050	.006	14989
138	28.2	.065	.115	.050		.002	.004	7949
139	28.2	.051	.104	.053		.010	.008	15103
140	28.3	.127	.074	.047		.014	.009	14985
141	28.5	.059	.105	.046		.004	.008	15124
142	28.7	.055	.069	.014		.004	.011	15152
143	28.7	.066	.114	.048		.000	.008	14992
144	29.0	.060	.092	.032		.000	.014	14960
145	29.0	.063	.083	.020		.014	.007	14963
148	29.5	.047	.059	.012		.004	.015	14956
149	29.5	.069	.122	.053		.010	.006	7948
150	29.5	.068	.124	.056		.008	.000	7954
151	29.6	.033	.066	.033		.000	.020	14954
152	29.7	.046	.099	.053		.010	.011	14979
153	29.7	.065	.130	.065		.025	.004	14959
154	29.9	.083	.099	.016		.025	.003	15133
157	30.1	.068	.084	.016		.007	.008	15108
158	20.1	.141	.194	.053		.002	.023	14983
159	30.2	.073	.097	.024		.023	.010	14964
160	30.3	.096	.133	.037		.002	.022	15128
161	30.4	.053	.079	.026		.001	.013	14953

Table 19 Continued

Reference Number	Moisture equivalent	Depression: Bouyoucos procedure	Depression: packed into place	Difference due to packing into place: Increase	Difference due to packing into place: Decrease	Difference between duplicates: Bouyoucos procedure	Difference between duplicates: Packed into place	Laboratory Number
		°C	°C	°C	°C	°C	°C	
163	30.6	.071	.114	.043		.004	.028	14952
164	30.7	.068	.125	.057		.017	.005	14991
165	30.8	.050	.073	.023		--	.010	14957
166	30.8	.065	.117	.052		.026	.010	14966
167	30.8	.103	.114	.011		.006	.008	14976
168	30.8	.090	.152	.062		.006	.008	7958
169	31.0	.068	.108	.040		.004	--	15143
170	31.0	.064	.104	.040		.009	.013	14967
171	31.3	.061	.111	.050		.022	.000	14965
172	31.4	.050	.109	.059		.003	.017	14958
173	31.4	.065	.086	.021		.002	.008	14995
174	31.4	.243	.250	.007		.015	.005	14988
175	31.7	.060	.072	.008		.004	.008	15139
176	31.7	.084	.122	.038		--	.007	14994
177	31.9	.049	.135	.086		.012	.006	14995
179	32.2	.056	.093	.037		.009	.006	15104
180	32.2	.056	.120	.064		.010	.006	15120
181	32.4	.066	.152	.086		.002	.000	15126
182	32.4	.105	.164	.059		.001	.008	7959
183	32.5	.063	.093	.030		.004	.011	15122
184	32.5	.079	.119	.040		.006	.004	7957
185	32.6	.145	.183	.038		.010	.011	14983
186	32.8	.124	.118		.006	--	.004	14975
187	33.1	.064	.094	.030		.015	.011	15109
188	33.1	.087	.098	.011		.011	--	14993
189	33.4	.066	.084	.018		.026	.009	15110
190	33.4	.102	.100		.002	.017	.011	14981
192	33.6	.066	.092	.026		.001	.000	15106
93	33.8	.048	.066	.018		.005	.011	14977
194	33.9	.050	.083	.033		.002	.013	15119
195	34.1	.074	.081	.007		.000	.003	15112
196	34.1	.104	.083		.017	--	.005	15113
197	34.2	.063	.100	.037		.003	.010	15105
198	34.8	.063	.117	.054		.004	.013	14990
199	35.0	.160	.180	.020		.010	.016	14987
200	35.3	.145	.186			.011	.000	14982
201	35.3	.102	.131	.029		.002	.010	7956
202	35.4	.053	.110	.057		.008	.007	15121
203	35.6	.073	.117	.074		.005	.003	14986
204	36.1	.075	.116	.041		.002	.002	7953
205	36.3	.054	.079	.025		.018	.007	14978
206	36.4	.064	.070	.006		.050	.010	14948
207	36.4	.140	.195	.055		.023	.010	14997
210	36.8	.130	.129		.001	.006	.003	15127
212	37.0	.067	.163	.096		.030	.012	14946

Table 19 Continued

Reference Number	Moisture equivalent	Depression		Difference due to packing into place		Difference between duplicates		Laboratory Number
		Bouyoucos Procedure	Packed into place	Increase	Decrease	Bouyoucos Procedure	Packed into place	
		°C	°C	°C	°C	°C	°C	
213	37.0	.117	.147	.030		.011	.020	14974
214	37.1	.057	.128	.071		.000	.012	15125
215	37.3	.055	.089	.034		.001	.007	15118
216	37.9	.083	.079		.004	.018	.007	15129
217	38.0	.063	.102	.039		--	.004	7604
218	38.0	.105	.246	.141		.070	.034	14947
219	38.3	.057	.093	.046		.006	.005	15107
220	38.6	.079	.119	.040		--	.002	15114
221	38.7	.093	.115	.022		.016	.010	15130
222	38.7	.055	.136	.081		.001	.008	15123
223	38.8	.068	.086	.018		.006	.012	15111
224	39.3	.065	.125	.060		.030	--	14949
225	39.7	.067	.080	.013		.005	.007	15116
226	39.9	.109	.118	.009		.006	.004	14975
227	40.7	.090	.149	.059		.020	.012	14950
228	40.7	.117	.141	.024		.003	.002	7595
231	41.3	.078	.148	.070		.018	.007	14945
232	41.8	.092	.132	.040		.004	.005	7599
233	42.2	.127	.149	.022		--	.016	14951
234	42.2	.103	.129	.026		--	.008	15131
236	43.8	.112	.132	.020		.001	.013	15117
237	44.0	.061	.111	.050		.003	.008	7952
239	45.4	.077	.105	.028		.006	.025	7590
240	45.7	.089	.110	.021		.005	.000	15115
243	46.9	.052	.079	.027		.004	.007	16175
250	63.1	.053	.078	.025		.025	.008	16170
252	64.0	.026	.080	.054		.005	.010	16185
253	64.5	.037	.082	.045		.001	.003	16190
264	129.5	.042	.074	.032		.004	.006	16180
265	180.5	.037	.062	.025		.004	.017	Peat 3
266	186.7	.046	.032		.014	.006	.006	" 2
267	193.5	.059	.043		.016	.017	.010	" 1
268	199.5	.032	.076	.044		.002	.011	" 4

Table 20 - Freezing point of samples frozen by Bouyoucos' method compared with that of samples packed tightly about the thermometer bulb.

Reference Number	Moisture equivalent	Freezing point depression		Difference due to intentional compression		Laboratory Number.
		Bouyoucos method	Packed about thermometer	increase	decrease	
		°C	°C	°C	°C	
10	3.0	0.092	0.131	.039		16189
11	3.3	.074	.065		.009	16188
13	3.7	.052	.048		.004	16194
14	3.7	.072	.028		.044	16195
22	4.7	.069	.048			
24	5.1	.039	.038		.001	16193
30	6.3	.049	.033		.016	16187
38	7.4	.032	.073	.040		16183
42	8.7	.071	.036		.035	16192
44	8.9	.042	.054	.012		16182
46	9.0	.042	.072	.030		16186
47	9.3	.098	.058		.040	16155
49	9.5	.042	.043	.001		16156
50	9.5	.057	.051		.006	16157
51	9.5	.059	.060	.001		16154
56	10.4	.042	.034		.008	16181
59	11.8	.033	.066	.033		16184
65	12.8	.029	.062	.033		16176
82	18.1	.056	.050		.006	15144
83	18.4	.043	.076	.033		7963
86	19.7	.044	.068	.024		15135
89	20.8	.044	.065	.021		7965
90	20.8	.054	.097	.043		7967
92	21.2	.054	.083	.029		7966
93	21.8	.049	.032		.017	15137
97	22.1	.035	.052	.017		15151
98	22.1	.040	.056	.016		15152
101	22.6	.046	.061	.015		7961
103	22.8	.044	.068	.024		7969
106	23.2	.048	.066	.018		7970
109	24.0	.050	.074	.024		7962
110	24.0	.069	.070	.001		7964
113	24.3	.055	.060	.005		7968
115	24.5	.041	.056	.015		7960
116	24.6	.059	.052		.007	15140
120	25.0	.055	.045		.010	15141
122	25.5	.046	.057		.011	7955
123	25.6	.049	.040	.009		15138
124	25.8	.059	.070		.011	15142
126	25.9	.059	.085	.016		7950
128	26.0	.061	.105	.044		7951
130	26.3	.049	.048		.001	15136

Table 20 Continued

Reference Number	Moisture equivalent	Freezing point depression		Difference due to intentional compression		Laboratory Number
		Bouyoucos method	Packed about thermometer	increase	decrease	
		°C	°C	°C	°C	
131	26.5	.061	.065	.004		14962
132	26.6	.062	.068	.006		14996
133	27.0	.053	.072	.019		14961
134	27.0	.116	.132	.016		14971
135	27.1	.092	.084		.008	14972
136	27.8	.133	.120	.013		14970
137	28.0	.300	.255		.045	14989
138	28.2	.065	.090		.025	7949
139	28.2	.051	.048		.003	15103
140	28.3	.127	.145	.018		14985
141	28.5	.059	.089	.030		15124
142	28.7	.055	.056	.001		15152
143	28.7	.066	.058		.008	14992
144	29.0	.060	.080	.020		14960
145	29.0	.063	.050		.013	14963
149	29.5	.069	.100	.031		7948
150	29.5	.069	.073	.005		7954
153	29.7	.065	.055		.010	14959
155	29.9	.083	.085	.002		15133
157	30.1	.068	.058	.010		15108
158	30.1	.141	.150	.009		14984
149	30.2	.073	.075	.002		14964
160	30.2	.096	.072		.024	15128
161	30.4	.053	.042		.011	14953
163	30.6	.071	.067		.004	14952
164	30.7	.068	.066		.002	14991
165	30.8	.050	.049		.001	14957
166	30.8	.065	.083	.018		14966
167	30.8	.103	.122	.019		14976
168	30.8	.090	.098	.008		7958
169	31.0	.068	.083	.015		15147
170	31.0	.064	.089	.025		14967
171	31.3	.061	.076	.016		14965
172	31.4	.050	.055	.005		14958
173	31.4	.065	.068	.003		14995
174	31.4	.243	.220		.023	14988
175	31.7	.060	.052		.008	15139
176	31.7	.084	.058		.026	14994
177	31.9	.049	.065	.016		14955
179	32.2	.056	.045		.011	15104
180	32.2	.056	.071	.015		15120
181	32.4	.066	.103	.037		15126
182	32.4	.105	.108	.003		7959
183	32.5	.063	.072	.009		15122
184	32.5	.079	.076		.003	7957
185	32.6	.145	.145	.000	.000	14983

Table 20 Continued

Reference Number	Moisture equivalent	Freezing point depression		Difference due to intentional compression		Laboratory Number
		Bouyoucos method	Packed about thermometer	increase	decrease	
		oC	oC	oC	oC	
186	32.8	.124	.090		.034	14975
187	33.1	.064	.052		.012	15109
188	33.1	.087	.003		.084	14993
189	33.4	.066	.059		.007	15110
190	33.4	.102	.045		.057	14981
192	33.6	.066	.075	.009		15106
193	33.8	.048	.042		.006	14977
194	33.9	.050	.053	.003		15119
195	34.1	.074	.050		.024	15112
196	34.1	.104	.055		.049	15113
197	34.2	.063	.075	.012		15105
198	34.8	.063	.067	.004		14990
199	35.0	.160	.145		.015	14987
200	35.3	.145	.142		.003	14982
201	35.3	.102	.099		.003	7956
202	35.4	.053	.074	.021		15121
203	35.6	.073	.081	.008		14986
204	36.1	.075	.080	.005		7953
205	36.3	.054	.037		.017	14978
206	36.4	.064	.063		.001	14948
207	36.4	.140	.150	.010		14997
210	36.8	.130	.091		.039	15127
212	37.0	.067	.130	.063		14946
213	37.0	.117	.094		.023	14974
214	37.1	.057	.100	.043		15125
215	37.3	.055	.058	.003		15118
216	37.9	.083	.056		.027	15129
217	38.0	.063	.085	.022		7604
218	38.0	.105	.143	.038		14947
219	38.3	.057	.080	.023		15107
220	38.6	.079	.088	.009		15114
221	38.7	.093	.108	.015		15130
222	38.7	.055	.098	.043		15123
223	38.8	.068	.060		.008	15111
224	39.3	.065	.083	.018		14949
225	39.7	.067	.050		.017	15116
226	39.9	.109	.090		.019	14975
227	40.7	.090	.135	.045		14950
228	40.7	.117	.113		.004	7595
231	41.3	.078	.083	.005		14945
232	41.8	.092	.100	.008		7599
233	42.2	.127	.135	.008		14951
234	42.2	.103	.095		.008	15131
236	43.8	.112	.105		.007	15117
237	44.0	.061	.090	.029		7952
239	45.4	.077	.070		.007	7590

Table 20 continued

Reference Number	Moisture Equivalent	Freezing point depression		Difference due to intentional compression		Laboratory number
		Bouyoucos method	Packed about thermometer	increase	decrease	
		°C	°C	°C	°C	
240	45.7	.089	.067		.022	15115
243	46.9	.052	.056	.004		
250	63.1	.053	.069	.016		16170
252	64.0	.026	.050	.024		16185
253	64.5	.037	.050	.013		16190
264	129.5	.042	.049	.007		16180
265.	180.5	.037	.062	.025		Peat 3
266	186.7	.046	.032		.014	" 2
267	193.5	.059	.045		.015	" 1
268	199.5	.032	.076	.044		" 4
Average 142 samples		.073	.077	Average of 83 = .-18	Average of 59 = .016	

SIMILARITY OF THE DATA SECURED BY BOUYOUCOS' METHOD TO THOSE WHEN THE THERMOMETER IS INTENTIONALLY COMPRESSED

Of the 142 samples intentionally subjected to the error from compression of the thermometer bulb, 83 showed greater depression than the same samples when frozen with the Bouyoucos method the average difference being .018°C; and 59 showed less, the average, difference being 0.016°. The average for all is .073°C by Bouyoucos method, and .077°C for the samples packed about the thermometer bulb. This close correspondence between the averages indicates quite clearly that the Bouyoucos method as here understood and followed is subject to error due to compression of the thermometer bulb. This compression was brought about in the cases where it was intentional, by packing the soil about the thermometer bulb after it was in place: in the Bouyoucos method the same result is brought about by pressing the bulb into the moist soil, and thus forming a cushion of the soil between the thermometer bulb and the wall of the freezing point tube. This soil may be so unyielding as to deform the thin walled bulb. The amount of deformation will vary with the stiffness of the moist soil, and that in turn with both the amount of water present and the nature of the soil.

Bouyoucos' practice with sticky samples was that of molding the "sample into a round elongated stick and dropping it into the tube," before introducing the thermometer (see 20, page 9), which was inserted into the soil (20, page 8). This procedure is excellently adapted to compress the thermometer bulb and thus influence the observed freezing point.

CONCORDANCE OF DUPLICATE DETERMINATIONS OF FREEZING POINT.

Bouyoucos presents no data on the concordance of freezing point determinations made upon duplicate samples, merely stating (19 P. 13) "The duplicate determinations of different samples of the same soil, however, would agree very closely, even with the latter (clay and loam) soils". He often mentions duplicate determinations of the same sample, meaning, however, successive freezings of the same portion, and found consistant differences in such cases, the depressions becoming less with freezings subsequent to the first. The difference was often only a few thousandths of a degree, but as he attached considerable importance to this slight change, it seems probably that it was greater than the usual difference between the depressions for duplicate portions of the same soil.

Hoagland reports a small number of duplicate determinations which he states ate typical. The data of his table from J. Ag. Res. XII. P 370, are here reproduced.

Soil No. Freezing point depression °C.

	Determination 1	Determination 2	Determination 3	Determination 4	Difference
10A	0.065	0.062			0.003
1B	.066	.069			.003
15A	.049	.052	.043	.050	.009
4B	.157	.157			.000

In the writer's study the difference found between the values for duplicate portions of a soil was often greater than those reported by Hoagland.

In order to determine the concordance of determinations, as well as to further define the effect of the compactness of the moist soil upon the freezing point, 5 mineral soils, and one peat were selected for a series of seven or eight freezings of similar portions.

The mineral soils were selected so as to give considerable range in texture, and also in tenacity in the moist condition. The samples were brought to the moisture equivalent in the usual way, 8 cups of each soil being centrifuged at one time so as to provide material for the larger number of freezings. The soil at the end of the centrifuging was removed from the cups, thoroughly mixed, and 16 portions placed in the freezing point tubes for freezing while two portions were weighed for duplicate moisture determination. One half of the portions of each sample in the freezing point tubes were kept as loose as possible by avoiding packing, and by tapping or jarring the tube while held in a horizontal position. Even with this treatment the two soils, B and C, which were selected for the reason that they had been observed to be sticky when moistened, were not loose, but consisted rather of lumps of compact soil.

The other halves of the portions were packed into place in the bottoms of the tubes, using the packing rod above described to protect the thermometer from compression.

The data on the freezing point depression of these similar portions under both conditions of packing are given in table 21,

Table 21 - Difference in freezing point between replicate portions of soil wet to the moisture equivalent by centrifuging, when frozen loose and when tightly packed with thermometer bulb protected from compression.

Soil	Condition	Moisture equivalent	Freezing point depression Portion 1	2	3	4	5	6	7	8	Average	Extreme difference	Difference due to packing
A	Compacted	4.8	.0.162	.180	.162	.198	.162	.170	.176	.198	.176	.036	.060
A	loose	4.8	.308	.184	.340	.188	.170	.150	.290	.260	.236	.190	
B	Compacted	13.3	.090	.068	.088	.093	.070	.078	.036		.082	.025	.002
B	loose*		.074	.090	.072	.065	.078	.088	.090		.080	..025	
C	Compacted	21.2	.120	.128	.176	.173	.142	.150	.162		.150	.056	.003
C	loose*	21.2	.190	.180	.156	.122	.148	.142	.130		..153	.168	
D	Compacted	23.8	.075	.082	.086	.085	.088	.074	.078		.081	.012	.009
D	loose	23.8	.063	.074	.078	.076	.070	.068	.075		.072	.015	
E	Compacted	26.7	.168	.180	.182	.170	.180	.170	.178	.165	.174	.017	.008
E	loose	26.7	.152	.122	.150	.145	.162	.168	.158	.160	.182	.046	
F (peat)	compacted	131.0	.059	.057	.055	.060	.052	.065	.052	.060	.057	.013	.013
F	loose	131.0	.061	.077	.065	.067	.071	.077	.063	.080	.070	.019	

* Samples are very sticky, and therefore the samples could not be gotten into any condition that could be compared to the loose condition of the more friable soils, such as D and E.

and show a range of .012 to .056°C among the freezings for the compacted portions and of .015 to .190 for the loose portions. This extremely great range for the loose would be much reduced if A, a sandy soil were rejected. It has been shown that such soils may not give correct freezing points, due to the small amount of water they carry, together with their slow freezing. The loose portions would naturally be more subject to error from slow freezing. Even rejecting this soil, the range is considerably more than would be expected from Bouyoucos' or Hoagland's statements, and as will be shown below, more than was usual for duplicates in the regular course of freezing of centrifuged samples in other parts of this study.

Table 22 - Summary of average freezing point depressions by Bouyoucos method, with difference between duplicates, for samples grouped by moisture equivalent.

Range of Moisture equivalent	Number of samples	Freezing point depression			Divergence between individual determinations		
		greatest	smallest	average for group	greatest	least	average
		°C	°C	°C	°C	°C	
1.5- 2.9	5	.452	.167	.313	.055	.005	.030
3.0- 4.9	5	.092	.052	.072	.022	.001	.004
5.0- 6.9	4	.077	.039	.057	.018	.001	.010
7.0- 8.9	3	.071	.032	.048	.020	.003	.005
9.0- 10.9	9	.098	.025	.049	.026	.005	.010
11.0- 12.9	2	.033	.029	.031	.004	.002	.003
13.0- 15.9	2	.049	.033	.041	.004	.002	.003
16.0- 18.9	4	.056	.032	.041	.008	.001	.005
19.0- 21.9	7	.054	.044	.048	.021	.002	.008
22.0- 24.9	12	.069	.035	.048	.010	.000	.004
25.0- 27.9	13	.133	.046	.069	.010	.002	.009
28.0- 30.9	27	.300	.033	.079	.050	.000	.008
31.0- 33.9	24	.243	.049	.080	.032	.001	.009
34.0- 36.9	14	.160	.053	.093	.036	.000	.010
37.0- 39.9	14	.117	.055	.082	.064	.000	.016
40.0- 45.9	10	.127	.061	.095	.070	.001	.010
46.0- 69.9	4	.052	.026	.042	.010	.001	.005
70.0- 99.9							
100.0-200.0	5	.059	.032	.043	.017	.002	.007

CONCORDANCE OF DUPLICATE DETERMINATIONS OF FREEZING POINTS FOR A SERIES OF SAMPLES FROZEN TO COMPARE THE METHODS.

The duplicate determinations of freezing-point depression in the case of all samples frozen by the Bouyoucos method, and later by the modified method described above, have been assembled in 18 groups in order of the moisture equivalents, and the summarized data in regard to divergence of pairs of duplicate determinations are reported by groups in tables 22, 23. The maximum divergence between duplicate portions of the same sample varied from nothing to .070°C.

The average divergence between duplicates is much the same whichever method is chosen. The extreme maximum divergence, however, is more frequent with the Bouyoucos method. Using it, maximum divergences as great as .030° are found in 6 of the 18 groups while only two groups show so great a difference by the modified method. The showing of the modified method becomes even more favorable when the magnitude of the average divergence is compared with that of the average depression. Since the average divergence is no greater, but the average depression by the modified method is greater, the percentage of depressions represented by the divergence is less with the latter method.

Table 23 - Summary of average freezing point determinations by modified method, with difference between duplicates, for samples grouped by moisture equivalent.

Range of Moisture Equivalent	Number of samples	Freezing point depressions			Divergence of duplicate		
		greatest	least	average for group	greatest	least	average
		°C	°C	°C	°C	°C	°C
1.5- 2.9	5	.441	.179	.307	.055	.010	.026
3.0- 4.9	5	.189	.090	.113	.017	.005	.009
5.0- 6.9	4	.096	.075	.083	.014	.007	.009
7.0- 8.9	3	.093	.077	.088	.010	.006	.007
9.0- 10.9	9	.111	.057	.081	.013	.003	.008
11.0- 12.9	2	.098	.093	.095	.010	.008	.009
13.0- 15.9	2	.049	.036	.042	.010	.009	.009
16.0- 18.9	4	.105	.051	.074	.010	.004	.006
19.0- 21.9	7	.136	.060	.091	.017	.004	.008
22.0- 24.9	12	.101	.062	.081	.011	.002	.007
25.0- 27.9	13	.200	.051	.115	.023	.002	.008
28.0- 30.9	27	.306	.059	.116	.028	.000	.010
31.0- 33.9	24	.250	.066	.115	.018	.000	.008
34.0- 36.9	14	.195	.070	.121	.016	.002	.007
37.0- 39.9	14	.246	.079	.130	.034	.002	.012
40.0- 45.9	10	.149	.105	.130	.025	.000	.010
46.0- 69.9	5	.110	.079	.086	.010	.003	.007
70.0- 99.9							
100.0-200.0	5	.076	.032	.057	.017	.002	.007

The percentage for each group, obtained upon dividing the average difference between duplicates by average freezing point depression is as follows:

Group	Bouyoucos Method	Modified Method.
1.5 to 2.9	10	8
3.0 to 4.9	6	8
5.0 to 6.9	18	11
7.0 to 8.9	10	11
9.0 to 10.9	20	10
11.0 to 12.9	10	10
13.0 to 15.9	7	21x
16.0 to 18.9	12	8
19.0 to 21.9	17	9
22.0 to 24.9	8	9
25.0 to 27.9	13	7
28.0 to 39.0	10	9
31.0 to 33.9	11	7
33.0 to 36.9	11	6
37.0 to 39.9	19	9
40.0 to 45.9	11	8
46.0 to 69.0	12	8
100.0 to200.0	16	12

Since the average divergence is no greater, but the average depression by the modified method is greater, the percentage of depressions represented by the divergence is less with the latter method. The one case where the experimental results are quite contrary to this statement, (X) is based upon a group of only two samples.

STATISTICAL DISTRUBUTION OF DEPRESSION.

For statistical study of the freezing points determined by the two methods, the grouping of the samples by their moisture equivalents has been retained, while the depressions according to their magnitudes have been placed in 12 groups, the ranges of which vary from .020° for the ones where the most of the depressions fall, to .100° where there are fewer. Tables 24, 25, 26, 27.

Table 24. Frequency distribution of freezing point depressions determined by Bouyoucos method, among soils grouped according to moisture equivalent.

Range in Moisture Equivalent	Number of samples in group	Numbers of samples with freezing point depressio between limits.											
		0-.030	.031-.050	.051-.070	.071-.090	.091-.110	.111-.130	.131-.150	.151-.170	.171-.200	.201-.300	.301-.400	.400-
1.5- 2.9	5								1	1		1	2
3.0- 4.9	5			2	2	1							
5.0- 6.9	4		2	1	1								
7.0- 8.9	3				1	2							
9.0- 10.9	9	2	4	2		1							
11.0- 12.9	2	1	1										
13.0- 15.9	1	1											
16.0- 18.9	4		3	1									
19.0- 21.9	7		5	2									
22.0- 24.9	12		9	3									
25.0- 27.9	13		3	7		1	1	1					
28.0- 30.9	27		4	14	4	2	1	1			1		
31.0- 33.9	24		4	12	3	2	1	1			1		
34.0- 36.9	14			5	3	2	1	2	1				
37.0- 39.9	15			9	2	3	1						
40.0- 45.9	10			1	4	2	3						
46.0- 69.9	4	1	1	2									
70.0 99.0	0												
100.0-200.0	5		4	1									
Whole group 1.5-200.0	164	5	40	62	20	16	8	5	2	1	2	1	2

More than 88 percent of all the depressions by both methods taken together fall into the 6 contiguous groups with limits from .030°C to .150°. The median that is the depression that is greater than that for one half of the samples and less than for the other half, falls between .051° and .070 for the Bouyoucos method, and between .090 and .110 for the modified method.

There appears to be no significant difference between the methods reflected in the distribution of the depressions that fall either above or below these median lines. The only difference in depression that seems probably connected with the moisture equivalent is that the depression for the group of moisture equivalent 1.5 - 2.9 is much greater than that for groups with higher moisture equivalent. This has already been explained as due to lack of heat released in the freezing of the small amount of water frozen. Aside from these, the differences in depression between groups and of samples within the groups can probably be regarded as due to differences in concentration of the soil solution. In general the groups showing the greatest range in depression are those having larger numbers of samples, and those of finer texture which under natural conditions would have more variation in thoroughness of leaching. For several of these samples it has been shown that leaching brings down the freezing point depression to well below .100° (see below).

The increased depression found when the freezing point is determined by the modified method is shown in groups of both high and low moisture equivalent.

Table 25. - Frequency distribution of freezing point depressions dedetermined by the modified method, among samples grouped according to moisture equivalent.

Range in moisture equivalent	Number of samples in group	Number of samples in group with freezing point depression between limits. 0-.030	.030-.050	.051-.070	.071-.090	.091-.110	.111-.130	.131-.150	.151-.170	.171-.200	.200-.300	.301-.400	.401-
1.5- 2.9	5									1	2	1	1
3.0- 4.9	5			2	1	1			1				
5.0- 6.9	4			3	1								
7.0- 8.9	3				1	2							
9.0- 10.9	9		1	1	4	2	1						
11.0- 12.9	2					2							
13.0- 15.9	1		1										
16.0- 18.9	4			2	1	1							
19.0- 21.9	7			2	1	3		1					
22.0- 24.9	12			2	7	3							
25.0- 27.9	13			1	5		1	4	1	1			
28.0- 30.9	27			3	4	6	9	1	1	2		1	
31.0- 33.9	24			1	4	9	5	1	2	1	1		
34.0- 36.9	14			1	3	2	4	1		3			
37.0- 39.9	15				4	2	3	4	1		1		
40.0- 45.9	10					2	2	6					
46.0- 69.9	4				4								
70.0- 99.9	0												
100.0-200.0	5		2	1	2								
whole group 1.5-200.0	164		4	19	42	35	25	18	6	8	2	1	

[illegible]

The [illegible] significant [illegible]

[illegible]

[illegible]

[illegible]

Table 26 - Percentage frequency distribution of depressions by Bouyoucos' method among samples grouped according to moisture equivalent.

Range in Moisture equivalent	Number of samples in group	Percentage of group with depressions between limits 0- .030	.031- .050	.051- .090	.071- .090	.091- .110	.111- .130	.131- .150	.151- .170	.171- .200	.201- .300	.301- .400	.400
1.5- 2.9	5								20	20		20	40
3.0- 4.9	5			40	40	20							
5.0- 6.9	4		50	25	25								
7.0- 8.9	3				33	67							
9.0- 10.9	9	22	45	22		11							
11.0- 12.9	2	50	50										
13.0- 15.9	1	100											
16.0- 18.9	4		75	25									
19.0- 21.9	7		72	28									
22.0- 24.9	12		75	25									
25.0- 27.9	13		23	53		8	8	8					
28.0- 30.9	27		15	52	15	7	4	4			4		
31.0- 33.9	24		17	51	12	8	4	4			4		
34.0- 36.9	14			36	21	14	7	14	7				
37.0- 39.9	15			60	13	20	7						
40.0- 45.8	10			10	40	20	30						
46.0- 69.9	4	25	25	50									
70.0-100.0	0												
100.0-200.0	5		80	20									
Whole group 1.5-200.0	164	3	29	38	12	10	5	3	1	1	1	1	1

Table 27 - Percentage frequency distribution of depressions determined by modified method, among samples grouped according to moisture equivalent.

Range in moisture equivalent	Number of samples in group	Percentage of group with depression between limits 0- .030	.031- .050	.051- .070	.071 .090	.091- .110	.111- .130	.131- .150	.151- .170	.171- .200	.201- .300	.301- .400	.400
1.5- 2.9	5									20	40	20	20
3.0- 4.9	5			40	20	20			20				
5.0- 6.9	4			75	25								
7.0- 8.9	3				33	67							
9.0- 10.9	9		11	11	45	22	11						
11.0- 12.9	2					100							
13.0- 15.9	1		100										
16.0- 18.9	4			50	25	25							
19.0- 21.9	7			28	14	43		14					
22.0- 24.9	12			17	58	25							
25.0- 27.9	13			8	38		8	30	8	8			
28.0- 30.9	27			11	15	22	33	4	4	7		4	
31.0- 33.9	24			4	17	38	21	4	8	4	4		

Range in Moisture equivalent	Number of samples in group	Percentage of group with depression between limits 0-.030	.031-.050	.051-.070	.071-.090	.091-.110	.111-.130	.131-.150	.151-.170	.171-.200	.201-.300	.301-.400	.400
34.0- 36.9	14			7	21	14	29	7		21			
37.0- 39.9	15				27	13	20	27	6	6			
40.0- 45.9	10					20	20	60					
46.0- 69.9	4				100								
70.0- 99.9	0												
100.0-200.0	5		40	20	40								
whole group 1.5-200.0	164		2	12	25	21	15	11	4	5	2	1	1

FREEZING POINT DEPRESSION IN RELATION TO PRECIPITATION.

The Minnesota samples dealt with in this study may be considered in three groups.

1. Those from the extreme western part of the state (Lac Qui Parle Co.) where the precipitation is about 24 inches annually.

2. Those from the northeast central part (Aitkin County) with a precipitation of about 27 inches.

3. Those from a number of locations in the southern part of the state, where the precipitation varies considerably, becoming greater toward the east, with an average of about 28 inches.

The summarized data for these three groups, when frozen by the Bouyoucos method from Table 11 is presented as Table 28, while similar data by the modified method is presented in Table 28.

By both methods there is a slight difference in the average depression, that for Lac Qui Parle County, which is driest and where, therefore, leaching under natural conditions might be expected to be least, being greater than for Aitkin County. The difference is much smaller than the error in determination, but being made up from large numbers of determinations, the average may show a real difference in the soluble matter of the soils, due to difference in rainfall. The conclusion is, however, more open to question because most of the samples of low moisture equivalent are from Aitkin County while most of those of the higher moisture equivalents,(excluding the peats and vegetable molds) are from the other areas. After determinations had been made on the samples from the other areas, the Aitkin samples were selected in order to complete the range of moisture equivalents.

Table 28 - Freezing point depression determined by Bouyoucos method according to geographical distribution.

Number of samples	Group	Number of Samples	Lac Qui Parle number	average depression °C	Aitkin number	average depression °C	South Minnesota Number	average depression °C
.271	1.5- 2.9	9	0		9	.271	0	
.078	3.0- 4.9	14	0		14	.078	0	
.057	5.0- 6.9	11	0		11	.057	0	
.046	7.0- 8.9	11	0		11	.046	0	
.047	9.0- 10.9	13	4	.064	9	.039	0	
.035	11.0- 12.9	8	0	--	8	.035	0	
.046	13.0- 15.9	9	1	.049	8	.046	0	
.046	16.0- 18.9	8	3	.051	4	.042	1	.043
.044	19.0- 21.9	11	4	.044	1	.026	6	.048
.066	22.0- 24.9	25	5	.044	3	.061	17	.068
.067	25.0- 27.9	17	11	.071	0	--	6	.060
.077	28.0- 30.9	32	23	.080	1	.028	8	.075
.081	31.0- 33.9	26	23	.078	0	--	3	.098
.094	34.0- 36.9	17	13	.094	0	--	4	.094
.076	37.0--39.9	15	14	.083	0	--	1	.063
.095	40.0- 45.9	15	6	.100	0	--	9	.092
.077	46.0- 69.9	14	0	--	5	.040	9	.098
.069	70.0- 99.9	6	0	--	2	.049	4	.078
.046	100.0-200.0	7	0	--	7	.046	0	--
Average of all .075			107	.078	93	.070	68	.076

For the samples of the Lac Qui Parle area, freezing point depression generally increases from group to group with moisture equivalent, whether the determination is made by the Bouyoucos' or by the modified method. The same relation holds but is less striking in regard to the samples of the southern area. For the group of coarser textured samples from Aitkin county the change is in the opposite direction, freezing point depression becoming less as moisture equivalent increases. It has already been pointed out that the freezing point shown for the soils of very low moisture equivalent is probably incorrect. In table 29 if the two groups of lowest moisture equivalent be disregarded on that account, and the two of moisture equivalent from 13.0 to 18.9 be excluded because of the small number of samples, the averages for the four remaining groups would be nearly constant and somewhat below that for the Lac Qui Parle and southern areas, making the series for the state as a whole conform to the gradual increase shown by the finer textured soils.

Table 29 - Freezing point depression determined by the modified method according to geographical distribution.

Range	Number in group	Average depression for group	Lac Qui Parle Co. Number of samples	Depression	Aitkin County Number of samples	Depression	Souther Minnesota Number of samples	Depression
		°C		°C		°C		°C
1.5- 2.9	5	.307	0		5	.307	0	
3.0- 4.9	5	.113	0		5	.113	0	
5.0- 6.9	4	.083	0		4	.083	0	
7.0- 8.9	3	.088	0		3	.088	0	
9.0- 10.9	9	.081	4	.095	5	.069	0	
11.0- 12.9	2	.095	0	--	2	.096	0	
13.0- 15.0	2	.042	0	--	2	.042	0	
16.0- 18.9	4	.074	2	.071	1	.051	1	.105
19.0- 21.9	7	.091	2	.080	0	--	5	.101
22.0- 24.9	12	.081	4	.069	0	--	8	.088
25.0- 27.9	13	.115	10	.114	0		3	.116
28.0- 30.9	27	.119	22	.116	0		5	.122
31.0- 33.9	25	.115	23	.110	0		2	.142
34.0- 36.9	14	.121	14	.121	0		2	.122
37.0- 39.9	15	.120	14	.123	0		1	.102
40.0- 45.9	10	.130	6	.132	0		4	.122
46.0- 69.9	5	.086	0	--	5	.086	0	
79.0- 99.9								
100.0-200.0	5	.057	0		5	.057	0	
Average of all			101	.114	37	.109	31	.109

The increase might be due either to less complete leaching out of soluble matter by the natural precipitation or to the lesser degree of washing of the finer samples, incident to preparation of the samples for freezing by the centrifuging method. In Table 28 the data for the Aitkin County samples cannot be made to agree with those from the other areas even by such rather drastic exclusion as that shown for table 29.

DILATOMETER MEASUREMENTS AT THE MOISTURE EQUIVALENT.

Dilatometers of the pattern devised by Bouyoucos were secured in two sizes and calibrated as he advised (7 - P 12), using 5 cc. of distilled water, the remaining space in the instrument being filled with gasoline.

With eight soils the expansion on freezing when wet exactly to the moisture equivalent was determined. The samples were prepared by centrifuging away the excess water from the saturated soils which was accomplished in the three ways described above (pages 39-40).

After the centrifuging the samples thus moistened to the moisture equivalent were removed from the centrifuge, weighed and placed in the dilatometer. The instrument was then filled with gasoline, closed and placed in the freezing bath at the temperature specified (C-1.5°C) and the amount of gasoline adjusted by addition through the stem. When the dilatometer and contents had come to the temperature of the bath, shown by the level of gasoline in the stem coming to rest, the height of gasoline was noted and the freezing initiated by setting the instrument into a colder bath (-8°, or colder). When the freezing had begun (shown by rise of gasoline in the stem) the dilatometer was returned to the first freezing bath and left until the rising column of gasoline had again come to rest, showing that expansion had ceased and freezing was no longer progressing. The column was again read, and the increase over the first column recorded as the expansion in freezing. This expansion was multiplied by 10, the factor used by Bouyoucos, to compute the volume of water frozen, and the difference (total water less water frozen) is the unfrozen or "unfree" water. The factor used is recognized to be somewhat greater than other workers give, but seems near enough, in view of the uncertainty introduced by some other features of the method, and it simplified the computation.

The determination was not found so rapid or so simple as would be supposed from Bouyoucos' statement, nor the results so concordant.

The values (Table 30) obtained for the "unfree" water on different portions of the same soil prepared in the same way vary as much as the average difference between those treated differently. It cannot be said that there is any definite difference in the amount of unfree water due to the treatment of the sample.

Averaging the comparable determinations of the 70 made in this series, the results show, as Bouyoucos observed, a constant tendency for the "unfree" water to be greater in the finer types of soil, that is, unfree water and moisture equivalent rise together.

The ratio between unfree water and moisture equivalent is shown in table 31. Since there seems to be no significant difference in the unfree water due to the methods used in preparing the samples, the data from the three methods has been averaged for use in this table. The range in this ratio, from 46 percent to 66 is considerable. The average, 57.6% is not far from 55 percent of the moisture equivalent, the indirectly determined wilting point as given by Briggs and Shantz (27).

Much more confidence could be placed in the data if it were not for the extremely great range in the duplicate determinations. No definite statements have come to the writer's attention showing how close agreement between duplicates any other workers have been able to secure. Bouyoucos' confidence in the significance of the slight difference in expansion between successive freezings of the same

Table 30 - Unfree water in soils at their moisture equivalent.

Determination:	Soil descriptions	Moisture equivalent	Volume of water unfrozen (computed) Sample prepared.			Duration of saturation and of leaching	Volume of leachings.
			after usual method	after prolonged saturation	after thorough leaching		
			p.p.h.	p.p.h.	p.p.h.	days	cc.o
1	A. Surface 6 inches		---	2.65	3.50	1	1500
2	of Merrimac loamy		---	3.00	3.00	3	1500
3	sand		2.40	3.20	---	26	1500
4			---	2.28	2.70		1500
Average		4.4	2.40	2.78	2.70		
1	B. Surface foot of		3.80	3.15	4.80	2	2000
2	a red sandy loam		3.75	2.50	2.75	6	3000
3			----	4.00	2.80	15	2000
Average		6.0	3.78	3.22	3.52		
1	C. First foot of Fargo fine sandy loam		5.45	4.60	5.20	16	1500
2			----	----	6.35	--	1500
Average		11.8	5.45	4.60	5.78		
1	D. Fifth foot of a		7.15	3.15	6.45	4	1000
2	red fine sandy		7.10	7.30	7.40	2	1000
3	loam		----	8.35	6.56	9	1000
4			----	7.60	6.77	4	1000
Average		12.7	7.12	6.60	6.79		
1	E. First foot of a		7.05	14.70	11.45	3	2000
2	red loam		9.70	9.00	9.80	7	2000
3			----	----	14.60	9	2000
Average		18.9	8.38	11.85	11.95		
1	F. Eighth foot of		10.00	9.65	10.30	2	1500
2	red silt loam		9.20	9.25	11.70	2	2000
3			14.50	11.40	11.35	4	1000
Average		19.6	11.23	10.10	11.12		
1	G. Third foot of		----	14.00	17.05	4	500
2	red silt loam		14.80	14.70	12.80	2	1500
3			9.45	18.85	13.90	3	500
4			13.65	16.40	14.85	4	1000
Average		22.1	12.65	15.99	14.65		
1	H. Surface 6 inches		-----	12.10	19.00	10	1500
2	of Hempstead silt		18.40	17.50	18.50	2	1500
3	loam		13.50	12.00	10.80	4	1500
4			10.55	21.10	20.30	3	1500
5			8.30	-----	13.40	2	1500
Average		23.5	12.81	15.67	16.52		
Average for all determinations			9.40	9.69	9.59		

Table 31 - Relation of the "unfree" water to the moisture equivalent.

Soil	Moisture equivalent	Unfree water	Ratio unfree water x 100 / moisture equivalent
			percent
A	4.4	2.63	60
B	6.0	3.44	59
C	11.8	5.40	46
D	12.7	6.78	53
E	18.9	10.90	58
F	19.6	10.82	55
G	22.1	14.58	66
H	23.5	15.12	64
		Average	57.6

portions of soil seem to indicate that he had satisfied himself that such differences are greater than the error of determination. The only definite statement noted, however, occurs in his first paper (12-P 200) where he states "in the majority of cases the duplicate determinations of the same kind of soil would agree very closely. Occasionally, however, the disagreement would be quite appreciable." An equally strong commendation in speaking of the agreement in the determinations here reported would not be justified.

The amount of air present in the moist sample, either dissolved in the water, or undissolved, may have a bearing upon both the concordance of the supposed replicate determinations, and upon the value found for the unfree water.

Bouyoucos referring to the undissolved air in the soil mass advised the use of stirring and gentle suction for its removal, but recognized that some air remained, even after the use of these means. He concluded that the presence of this residue introduced no important error, but did not mention the possible effects of dissolved air, which if not present in the water used for moistening the samples, will be supplied by the air adsorbed upon the air dry soil particles, or from the undissolved air existing in the pores. That this dissolved air may have an effect upon the determination is shown by the following observation.

It was observed that when water was frozen in the dilatometer, even in the absence of soil, a gas, assumed to be air, was expelled. Even when this gas was allowed to escape from the instrument and the same portion of water frozen and thawed repeatedly, gas was expelled at each freezing. Thus the same 5 cc. portion of distilled water was observed to expel gas on 16 consecutive freezings in a period of four days, and the average volume of the expelled gas in the last four freezings was roughly only about one-tenth less that in the first four.

This ability of water to expel the gas at successive freezings may be due to the cold water abstracting dissolved air from the filling liquid (gasoline)*. From the above it appears that dissolved air will always be present in the solution when soils are frozen in the dilatometer. As the air expelled is likely to be entrapped within the soil mass, rather than to escape from the instrument, as it may when water alone is frozen, it will tend to produce an expulsion of the filling liquid that is not due to the increased volume of the water on freezing. Even if the gas should prove not to be air, this source of error may always be expected, though it is not possible from the data at hand to state how great it is, or whether it is relatively constant.

FREEZING POINT OF SOIL SOLUTIONS DISPLACED FROM THE SOIL, COMPARED WITH THAT OF THE SOIL BEFORE DISPLACEMENT.

A sample of Hempstead silt loam surface soil was used for the trials of displacement of the soil solution by alcohol as described by Parker (38).

The two or three kilograms of air dry soil needed for each trial was mixed with the desired amount of distilled water, and stored for several days in a large mouthed glass bottle closed with a cork stopper, before being packed into the glass percolators for the displacement. As Parker has pointed out, the method at times is somewhat slow; and considerable experience is required before satisfactory manipulation is secured. The chief difficulties are in deciding upon a suitable degree of moistness for the sample, in uniformly moistening to that desired degree the rather large samples required,

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* But few data on the solubility of the air in gasoline are easily found. St. Gniewosz and Al. Walfisz, Zeit. fur Phys. Chemie Vol. 1 P-70-72 give absorption coefficients for petrolium and water as follows:

	Petroleum		Water at	
	at 20°	at 10°	Content	10°
Nitrogen	0.117	0.135	1.15	0.0140
Oxygen	.202	.229	1.13	.0284

and state that petroleum is useless as a covering to protect from access of oxygen.

G. Just. Zeit for Phys Chemi Vol. 37 P-3420 gives for nitrogen in Xylol and in water. In Xylol 25° - 20°, in water 25° 20°
Nitrogen 0.1217 .1185 .01634 .01705
It thus seems probable that these air gases are more soluble in gasoline than in water, and hence could easily be able to furnish a considerable amount to be absorbed by the water.

and most difficult of all, in packing the moist sample into the percolator so evenly and compactly as to secure ready and uniform penetration of the alcohol used as the displacing agent. If the packing is carried too far the displacement is prevented or unduly delayed. If not far enough, channels are formed in the soil mass, which permit the alcohol to flow past the soil solution instead of forcing the latter downward before it so that it may be secured uncontaminated by the alcohol.

The first few successive portions secured had freezing points approximately constant for each soil sample Table 32, and were thus regarded as of constant concentration. This freezing point was above

Table 32 - Freezing point depression of Hempstead silt loam (moisture equivalent = 22.8), and of successive portions of solution displaced from it by alcohol.

Trail	Total water content	Depression for moist soil	Number of portion displaced	Volume of portions	Depression for portions of solution	Average	Difference in depression of soil and solution	Remarks
	p.p.h.	oC		cc.				
A	25.6	0.047	1	25	0.024)			
			2	25	.020)	.022	.025	
			3	130	.022)			
			4	25	.041)			
			5	25	.097)			alcohol in solution
			6	25	.209)			
			7	90	.915)			
B	22.0	.065	1	25	.037)			
			2	25	.040)	.038	.027	
			3	25	.038)			
			4	25	.128)			alcohol in solution
			5	25	.408)			
C	21.8	.076	1	25	.033)	.033	.043	
			2	25	.043)			
			3	25	.046)			alcohol in solution
			4	25	.071)			
			5	25	.143)			
			6	25	.303)			
D	21.6	----	1	25	.040	.040	---	
			2	25	.070)			alcohol in solution
			3	25	.185)			
			4	25	.380)			

Table 32 - Continued

Trial	Total water content	Depression for moist soil	Number of portion displaced	Volume of portions	Depression for portions of solutions	Average	Difference in depression of soil and solution	Remarks
E	21.0	---	1	50	.030)			
			2	50	.032)	.031		
			3	50	.031)			
			4	50	.077)			alcohol in solution
			5	50	.079)			
F	17.6		1	25	.045)			
			2	25	.050)	.049		
			3	25	.052)			alcohol in solution
			4	25	.083)			
			5	25	1.200)			
G	14.6		1	25	.058)	.064		
			2	25	.070)			
			3	25	.205)			
			4	25	.490)			
H	12.5		1	25	.057)	.063		
			2	25	.069)			
			3	25	.400)			alcohol in solution
			4	25	3.300)			

that of the moist soil before the displacement. In the case of the samples that gave a satisfactory volume of uncontaminated solution the depression was approximately proportional to the dryness of the samples from which they were displaced. All three of these observations confirm the findings of Parker, and correspondingly support his conclusion that the freezing points of such moist soils cannot be regarded as due only to the concentration of the solutions.

FREEZING POINTS OF SOIL MOISTENED WITH AQUEOUS ORGANIC SOLUTIONS INSTEAD OF WITH PURE WATER.

Parker has pointed out that if, as Bouyoucos concluded, soils carry "unfree" water that cannot act as a solvent, then dry soil, when moistened with a chemically inactive solution, should withdraw water from the solution, and render it unfree in the soil, while the solute would be concentrated in the portion of water remaining free. If such is the case the freezing point of a soil so moistened should be below that of the soil when equally moistened with pure water, by more than the depression of the solution before contact with the soil. If a soil moistened with a solution freezes below the same soil equally moistened with water by only the depression of the solution before

contact with the soil, it would indicate that no water has been withdrawn from the solution, and accordingly that there is no such "unfree water". Parker reported (41) such data from experiments with glycerine and alcohol in water solutions, using oven dried soil, and concluded that no water had been thus withdrawn from the moistening solutions. In addition he found that the liquid displaced from soil previously oven-dried and moistened with the same solutions, froze at temperatures that led to the same conclusion. To verify these results in respect to the freezing point the writer repeated the experiments, using glycerine and dextrose in aqueous solution.

Portions of Hempstead silt loam surface thoroughly dried in an oven, were treated with the desired amounts of the solutions, and mixed with them as rapidly as possible to avoid loss by evaporation. The small amount of water lost was later actually determined by drying the samples after the freezing points had been determined. In order to give time for distribution of the moistening solutions, the samples, in stoppered freezing point tubes, were stored for one day in the moist-air box before freezing. Table 33. The corrected depression made necessary by the evaporation from the sample during the mixing is reported in the fourth column. The portion of the observed depression due to the presence of the solute (Column 6) and of the amounts of "free" and "unfree" water indicated are computed from the determinations given above. The computations made as indicated in the foot note below the table, may be illustrated here, using for the illustration the sample treated with 24 parts of dextrose solution per hundred parts of dry soil.

COMPUTATION OF THE UNFREE WATER.

Although 24 p.p.h. of the solution was added, water evaporated during the preparation of the sample, so that only 22.55 p.p.h. were found after the freezing. Thus, the solution was concentrated by the loss of water, becoming stronger and therefore having a greater freezing point depression, in the ratio of $\frac{24.0}{22.5}$. The corrected depression then is $\frac{2400}{2255}$ x 0.380°C or 0.40°C.

The depression due to presence of the solute is found by subtracting the depression found with 24 p.p.h. water from that with the same amount of dextrose solution or .655 - .184 = 0.471°C.

Since the depression due to solute is greater than the corrected depression for the solution alone it indicates by Bouyoucos theory that some water has been withdrawn from the solution (made "unfree") and the solute concentrated in the remaining or "free" water. The amount is shown by the proportion $\frac{\text{corrected dpression}}{\text{depression due to solute}} = \frac{\text{free water (x)}}{\text{total water.}}$ The water not free to act as a solvent is the "unfree" column 8 indicated by the results, and found by subtracting "free" from the total amount of water.

Table No. 33 - Freezing points and "unfree" water of a soil first dried and then moistened with inert aqueous organic solutions.

1 Liquid added	2 Depression for liquid alone	3 Water found	4 Depression for liquid corrected for evaporation	5 Observed depression for moistened soil	6 Depression due to solute	7 Free water acting as solvent	8 "Unfree" water indicated
p.p.h.	°C	p.p.h.	°C	°C	°C	p.p.h.	
Water 24.0	0.000			0.184			
21.0	0.000			.225			
18.0	0.000			.280			
15.0	0.000			.381			
12.0	0.000			.617			
Dextrose 24.0	0.300	22.55	.406	.655	.471	19.4	3.1
21.0	0.380	20.60	.387	.722	.497	16.0	4.6
18.0	0.380	17.35	.396	.785	.505	13.6	3.7
15.0	0.380	15.40	.370	.860	.479	11.9	3.5
						Average	3.7
Glycerine 24	0.660	24.60	.644	.910	.726	21.8	2.8
21	0.660	21.65	.642	.984	.759	18.3	3.3
18	0.660	18.00	.660	.987	.707	16.8	1.2
15	0.660	14.75	.650	1.111	.730	13.7	1.1
12	0.660	12.15	.641	1.275	.658	11.8	0.3
						Average	1.7

Foot note: values arrived at as follows

1 Column 1 - measured
2 " - observed
3 " - determined
4 " - computed (Col 2 x $\frac{\text{Col 3}}{\text{Col 1}}$
5 " - observed
6 " - computed (Col 5 solution - Col 5 water)
7 " - computed $\left(\frac{\text{Col 4 x Col 3}}{\text{Col 6}}\right)$
8 " - computed (Col 3 - Col 7)

The data treated in this way indicates a small amount of unfree water for each determination made, the amount ranging from .3 to 4.6 p.p.h. and averaging about twice as much when dextrose is used for the solute as when glycerine is used. With glycerine the unfree water is higher where the larger amounts of solution were used, but such is not the case with the dextrose. The amounts of unfree water indicated, 0.3, to 4.6 p.p.h. are far below the 12.8 p.p.h. indicated by the dilatometer measurements reported for the same soil (sample H, Table 31).

It has already been pointed out that incomplete distribution may disturb the freezing point, and that distribution becomes slower as soils become drier. Some of these soils were wet to not much more than half the moisture equivalent which may help to explain the lack of uniformity in the amount of unfree water indicated in different portions of the same soil.

UNFREE WATER OF DRY SOIL OR IGNITED RESIDUE, MOISTENED TO THE MOISTURE EQUIVALENT WITH AQUEOUS ORGANIC SOLUTIONS.

Portions of the same soil (Hempstead silt loam) were ignited for one hour in a muffle-furnace, with loss on ignition of 6.15 percent. Samples of both the oven-dried soil and this ignited residue were moistened with excess of water and of the solutions of dextrose and of glycerine above described. The samples were centrifuged to the moisture equivalent, and portions dried to determine the moisture, content, while other portions were frozen withoug drying. As the samples were not later exposed to loss by evaporation, it was not necessary to determine the moisture after the freezing. "The "unfree" water (Table 34.) found for the unignited soil is less in the portion treated with dextrose solution than shown in Table 33, but for the ignited residues the amount is slightly higher than for the unignited soils. This is directly contrary to the observation of Bouyoucos (17) that generally no unfree water is present in ignited soil (estimated by dilatometer measurement) and if any is found, it is less than in the original soil. The difference is not great, and the data are too few for a definite conclusion.

Table 34 - Freezing point depressions and "unfree" water of Hempstead silt loam and of ignited soil residues moistened with aqueous organic solutions and then brought to moisture equivalent by centrifuging.

Sample	Liquid	1 and 3	2 and 4	5	6	7	8
		Moisture equivalent	Depression for liquid alone	Observed depression for moistened sample	Depression due to solute	Free water acting as solvent	Unfree water indicated
			°C	°C	°C	p.p.h.	
Dried soil	distilled water	22.8	0.000	0.090	- -	?	?
Ignited soil	residue water	17.0	0.000	0.081	- -	?	?
Dried soil	Dextrose solution	22.35	.380	.511	.421	20.2	2.2
Ignited soil	Residue solution	16.25	.380	.580	.499	12.4	3.8
Dried soil	Glycerine solution	21.75	.660	.802	.712	20.2	1.5
Ignited soil	Residue solution	15.30	.660	.850	.769	13.1	2.2

Footnote: Values arrived at as follows

1 and 3 column - determined
2 and 4 " - determined
5 " - observed
6 " - computed (depression col. 5 for solution - depression for water)
7 " - computed $\frac{\text{(Col 2 (or 4) x Col 1)}}{\text{Col 6}}$
8 " - computed (Col. 1 (or 3) - Col 7).

SUMMARY.

1. The experimental work reported includes determinations of moisture equivalents and of freezing points of over 300 Minnesota soils, including a series with a wide range in moisture equivalent, from less than 2 to 200, the interval between successive samples being small for the first 244. These were frozen after being prepared both by Bouyoucos' method and by saturating the dry soils and centrifuging away the excess water. The freezing was performed both by the Bouyoucos method and by two modifications of it. The expansion on freezing with a small number of samples was measured by the Bouyoucos dilatometer method, the soil solution was displaced by alcohol and the freezing point determined. Lastly dried and ignited soils were moistened with aqueous organic solutions, and their moisture equivalents and freezing points compared with those of the same materials made equally moist with pure water.

2. In the case of the moisture equivalents, duplicate determinations agreed well. The effect both of leaching and of prolonged contact of water with a soil, was to slightly increase the value. Ignition in every case caused a very marked decrease

3. With repeated freezing and thawing of the same portion of moist soil the freezing point depression was very slightly lowered when the water had been thoroughly mixed with the soil, but markedly increased when it had been simply added to the surface of the soil without mixing. The slight decrease in the first case is probably due to a compacting of the sample from withdrawing and returning the thermometer for the successive freezings, while the greater effect in the second case is due to the gradual advance of the moisture into the dry soil, the observed freezing point being really only that of the most readily frozen or wettest part.

4. At the moisture equivalent the depression is less, and more nearly constant when the soil is brought to this degree of moistness by saturating the air-dry sample and centrifuging away the excess of water than when the computed amount of water is mixed with the air-dry soil. The lessened depression is to be attributed to the loss of soluble matter in the water centrifuged away, and the greater uniformity to the more even distribution of the water.

5. Leaching caused but slight change in the freezing points of soils whose original depression was small, but marked reductions of depression with those where the original depression was large, in some cases amounting to more than fifty percent, due to the loss of soluble matter.

6. Prolonged contact with excess water, but without percolation, continued as long as the leaching, only slightly lessened the depression.

7. Ignition sometimes raised and sometimes lowered the freezing point at the moisture equivalent.

8. The freezing point depressions for the different soils at the moisture equivalent varies within much narrower limits than when a uniform amount of water is added to the air-dry samples, as practiced by Bouyoucos, that for soils of fine texture usually only very slightly exceeding that for those of coarse texture. Very coarse textured soils showed the greatest depression, but this is probably due to the amount of water frozen being too small to supply the heat required to raise the temperature of the moist soil to its actual freezing point. Aside from this the differences found were no greater than may be attributed to differences in the soluble matter content.

9. A study of the effect of packing upon the freezing point has led to the recognition of a cause of serious error in the method as hitherto carried out, in that the thermometer bulb is exposed to compression when inserted into the moist soil, and a modified method, avoiding this source of error, has been devised. Using the same soils a comparison was made of the Bouyoucos method with this improved method and a third in which the soil was purposely packed firmly about the thermometer bulb. With the last the depression was always less than with the second in which the thermometer bulb was protected. The data from the Bouyoucos method agreed more closely with those from the third method, where the thermometer was intentionally subjected to compression, than with those from the second. When compression of the thermometer bulb is guarded against compacting the sample usually lowers the freezing point.

10. Duplicates were frequently discordant when the soils were frozen in very loose condition. The concordance of duplicates was better with the degree of compactness incident to the Bouyoucos and the modified methods, the two being quite similar in this respect. The concordance on the whole was neither better nor worse for fine textured soils than for coarse textured.

11. The expansion on freezing of soils at the moisture equivalent was determined by dilatometer measurements. The amount of "un free water" they carried, computed from these data, varied considerably, being greater with finer soils, as found by Bouyoucos. The average for the soils frozen was not far from 55 percent of the moisture equivalent, thus agreeing with Bouyoucos' observation that the "unfree" water approximates the wilting coefficient as defined by Briggs and Shantz. The "unfree water" computed by the method proposed by Parker, was found to be very much less than that computed from the dilatometer readings, a result which gives some support to Fisher's argument that the expansion on freezing of capillary water is less than that of water in bulk.

12. Attention is called to a hitherto unrecognized error in the measurement of the expansion on freezing of soil water. This is due to the air dissolved in the soil solution.

13. Confirming Parker's observation, freezing point depressions of solutions displaced by alcohol from moist soils were found smaller than those for the moist soils themselves. The difference, however, when the solutions were displaced from soils wet about to the moisture equivalent was less than the constant value suggested by Parker as due to adhesion between soil and water (0.050°C). The total depressions for samples brought to the moisture equivalent by centrifuging were also found smaller than Parker's value for such a constant.

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Biographical Sketch.

Reuben Marion Pinckney was born near Macksberg, Iowa, on Dec. 3rd, 1880. His elementary education was secured in the public schools of Custer, Dawson, Buffalo and Valley counties, Nebraska.

University training and degrees.

Nebraska Wesleyan University, 1902-1906. Degree of Bachelor of Science, 1906, with major in Chemistry.

University of Nebraska, 1907-1908. Degree of Master of Arts, with major in Agricultural Chemistry.

University of Minnesota, 1922-1924. Degree of Doctor of Philosophy in December, 1924, with major in Soils, minor in Physical Chemistry.: Thesis title "The Freezing Point of Soil at the Moisture Equivalent".

Experience.

Student assistant in chemistry, Nebraska Wesleyan University, 1902-1905.

Assistant in chemistry, Nebraska Agricultural Experiment Station, 1907-1908.

Assistant Chemist, Montana Agricultural Experiment Station, 1908-1922.

Research Assistant, Minnesota Agricultural Experiment Station, 1922-1924.

Publications.

1. 1904 "On Certain Nitrogen Compounds". F. J. Alway and -----, Am. Chem. Jour. Vol. 32, p. 398-.
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